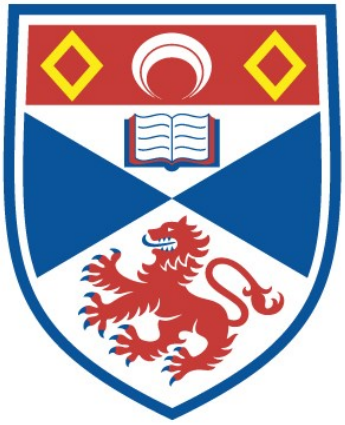
THE SYNTHESIS AND CHEMICAL PROPERTIES OF SOME COMPOUNDS CONTAINING THE PERINAPHTHENE NUCLEUS

William Bonthrone

A Thesis Submitted for the Degree of PhD
at the
University of St Andrews



1959

THE SYNTHESIS AND CHEMICAL PROPERTIES OF SOME COMPOUNDS CONTAINING THE PERHYDROTHIOPHENE NUCLEUS

being a Thesis presented by

WILLIAM BONTHRONE

to the University of St. Andrews in application for the degree of Ph.D.

Certificate.

I certify that William Bonthrone has spent nine terms at research work under my direction, that he has fulfilled the conditions of Ordinance No.16 (St. Andrews) and is qualified to submit the accompanying Thesis in application for the degree of Ph.D.

[redacted]

Director of Research.

25th May 1950.

DECLARATION.

I hereby declare that the following Thesis is a record of the results of experiments carried out by me, and further that the Thesis is my own composition and has not previously been presented for a higher degree.

The research was carried out in the Department of Chemistry, St. Salvator's College in the University of St. Andrews under the direction of Dr. D.H. Reid.

25th May, 1950.

UNIVERSITY CAREER.

I first matriculated in the United College of St. Salvator and St. Leonard, University of St. Andrews, in October, 1951, and subsequently graduated B.Sc. with First Class Honours in Chemistry in July, 1955.

I was admitted as a Research Student in the Department of Chemistry, United College, St. Andrews in October, 1955.

I was awarded a Post-graduate Scholarship by the University of St. Andrews covering the period of my research programme up to July, 1958 and for the months of January and February, 1959. During the months August to December, 1958, I held an award from the Carnegie Trust for the Universities of Scotland.

ACKNOWLEDGEMENTS.

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I am grateful to the University of St. Andrews and to the Carnegie Trust for the Universities of Scotland for financial help during the period of my research programme.

I should like to thank the members of the Technical Staff of the Chemistry Department in St. Andrews who gave of their services, especially to Mr. Z.M.Zochowski for help with the experimental aspect of the work and to Messrs. R. Morris and I. Hayes for carrying out the photography required for the presentation of this thesis. I am indebted to Mrs. M.Zochowski who undertook the typewriting of the manuscript.

My thanks are also extended to Professor John Read, F.R.S., for his permission to carry out these researches in the Chemistry Department, University of St. Andrews.

EXPLANATORY NOTE.

This thesis comprises three parts, Parts A,B and C. Each part is divided into a number of principal sections prefixed by Roman numerals, and these sections are divided into sub-sections prefixed by Arabic numerals. Two sub-sections (B,II,2 and B,II,3) have been further divided, each division being indicated by a letter e.g. B,II,3 (c) - The Oxygenation of Perinaphthyl.

Part A commences with a very brief survey based on the chemical literature of the concept of aromaticity. A number of excellent reviews covering both the historical and theoretical aspects of this subject have appeared recently and, in view of this, a more detailed consideration of aromaticity was deemed unnecessary. This is followed by a discussion of the chemistry of the annulenes with particular emphasis on the theoretical aspects of the subject. The chemistry of perinaphthene and its derivatives is then reviewed in detail and this leads logically to a reasoned description of the aims of the experimental investigation.

Part B is a discussion of the results achieved in the course of investigations centred on the perinaphthene nucleus. Part C is devoted entirely to a description of experimental details, and is the complement to Part B.

Where reference is made to the chemical literature, this is indicated by a number in parenthesis and superscript, a key to which is to be found at the end of the thesis under the section headed "Literature Cited".

CONTENTS.

PART A.

* * * * * * * * * * * * * * *

PART B.

Contents continued: Page.

Contents continued: Page.

* * * * * * * * * * * * * * * *

PART C.

Contents continued: Page.

Contents continued: Page.

Contents continued:

Contents continued: Page.

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PART A

A. I Aromatic Stability and the Azulene Nucleus.

A. I. 1. Introduction.

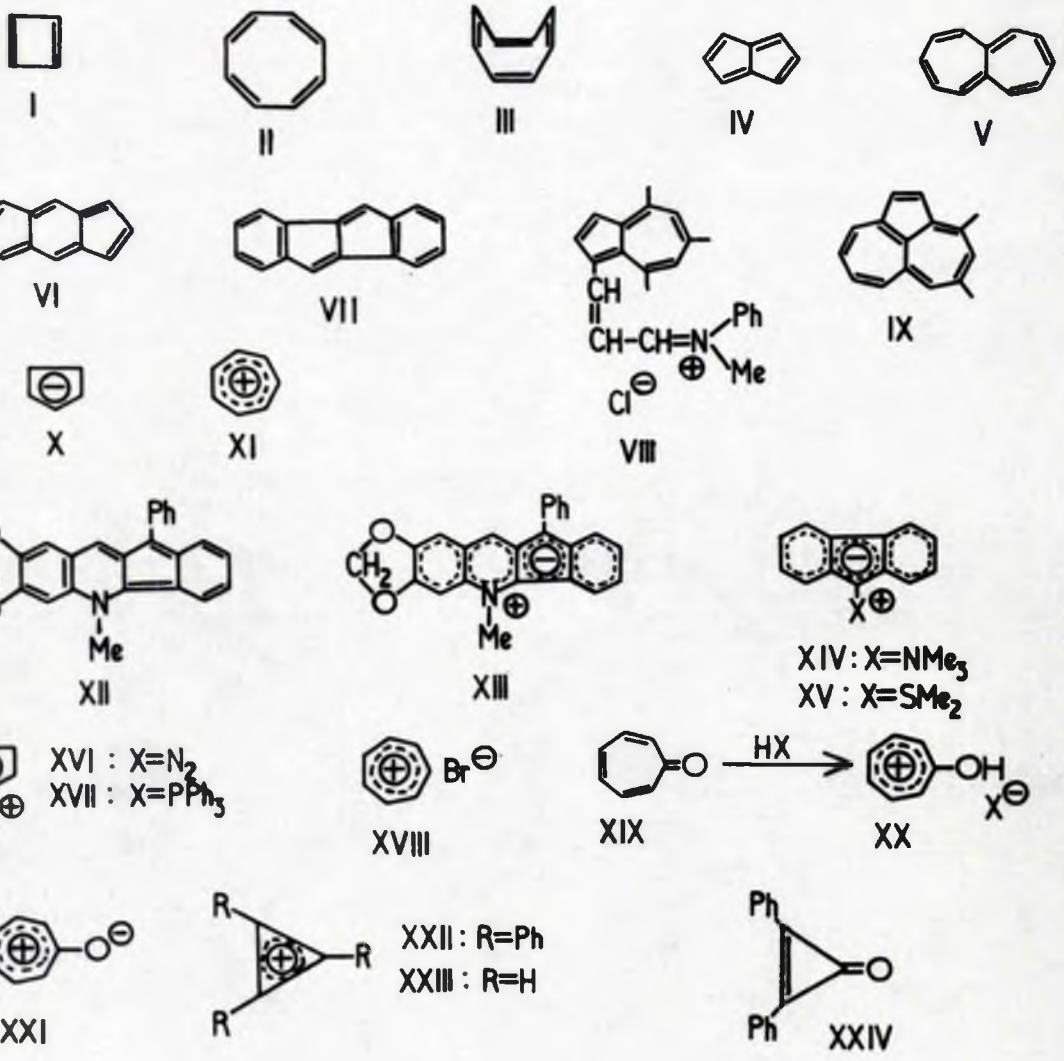
In 1865, in his classical papers on the constitution of aromatic compounds, Kekulé[1] proposed the well-known cyclic structure for benzene and suggested that the peculiar properties of the aromatic compounds are dependent on the properties of this ring system. From the point of view of the nature of aromaticity, benzene is important in that it is both the parent and the simplest member of the aromatic series of compounds and its properties may be taken as representative of those of the aromatic compounds. Of these properties, its general stability and its marked preference for reacting by substitution rather than by addition are the outstanding features most closely related to its physical structure. It is also characteristic of the aromatic compounds that they are readily formed by dehydrogenation reactions. Aromatic character is reciprocated by the characteristic and easily recognised properties of nuclear substituents such as hydroxyl, amino and aldehyde groups, properties which are not usually exhibited in combination with an aliphatic nucleus.

One important interest of the aromatic compounds lies, for the theorist, in the structural problems they present and, for the experimentalist, in the attempts to verify theoretical predictions that certain conjugated systems will be stable or "aromatic" while others will not.

Kekulé's description of benzene, consisted in his recognition that the second half of a benzenoid double bond cannot be assigned a unique position in the molecule; the physical meaning of this was not fully understood until the advent of the electronic theory of valency and its application to aromatic molecules.

The structure of benzene was first discussed in detail by Hückel[2] who employed two approaches to the problem, the molecular orbital approach which had been invented somewhat earlier by Lennard-Jones and has been developed since by Hund, Mulliken and Coulson, and the valency bond method which has been developed by Pauling and Wheland. Hückel[3] showed that the binding energies of molecular orbitals in cyclic systems generally, will be at a maximum in rings containing two or six π-electrons; electron systems of ten, fourteen, etc. π-electrons would also be unusually stable by virtue of possessing fully-filled molecular-orbitals with considerable delocalisation energy if planar rings of this size were sterically possible. This is the basis of the familiar Hückel rule that aromatic character will be shown in cyclic conjugated rings containing $(4n + 2)\,\pi$-electrons, where n is integral. In this way, the peculiar stability of the "aromatic sextet" can be understood; the special nature of this arrangement of electrons was recognised[4] in both the carbocyclic and heterocyclic series of aromatic compounds, although it was not interpreted by the classical theory.

Since its formulation, Hückel's theory of aromaticity has been


I
II
III
IV
V
VI
VII
CH
CH-CH=N
Ph
Me
Cl⊖
IX
X
XI
VIII
Ph
CH2
O
N
Me
XII
XIII
X⊕
XIV: X=NMe3
XV: X=SMe2
XVI : X=N2
XVII : X=PPh3
Br⊖
XVIII
HX
OH
XIX
XX
XXI
R
XXII : R=Ph
XXIII : R=H
XXIV

strengthened by the accumulation of experimental evidence. The completely conjugated mono- and polycyclic hydrocarbons support, in their chemical behaviour, the predictions of stability based on molecular-orbital calculations. Cyclobutadiene (I), which theoretical considerations indicate should possess no aromatic properties[5] has resisted all attempts to synthesise it[6],[7],[8]. Cyclooctatetraene (II), first synthesised by Willstätter and Waser[9], has been investigated by several different techniques including X-ray analysis[10] electron-diffraction[11] and infra-red and Raman spectral analysis[12]. All show that the molecule is non-planar and exists in a "tub" form (III) with alternate single and double bonds. This molecule is therefore irrelevant to the theory of aromaticity since non-planarity prohibits effective delocalisation of the π-electron system over the molecule. The compounds (IV) to (VI), in which the number of carbon atoms providing π-electrons is a multiple of four, are not expected to show aromatic character; in accord with this, all attempts to synthesise these compounds have failed[13], [14], [15], [16] and the somewhat unstable dibenzpentalene (VII) shows purely olefinic properties in the central diene system[17].

A heptalene derivative, 2,4-dimethyl-1,10-cyclopentenoheptalene (IX) has recently been synthesised[18] by treatment of the azulene immonium salt (VIII) with alcoholic alkali. The preliminary account of the properties of this dark red crystalline compound indicate that it is stable and shows aromatic character. Thus it undergoes

formylation by the Vilsmeier method and acetylation in the Friedel-Crafts reaction. However, its stability is probably due to a considerable contribution from structures of the azulene type and it is more accurate to represent the hydrocarbon as a 1,8-cycloheptenoazulene derivative rather than a 1,10-cyclopentenocheptalene derivative. This is supported by the fact that the hydrocarbon is reversibly soluble in 50% sulphuric acid, a property characteristic of the azulenes (A,I,2).

With five- and seven-membered monocycles, the theoretical predictions were definite[2],[19]; that the conjugated six π-electron systems present in the cyclopentadienide anion (X) and the cycloheptatrienylium cation (XI) should be stable whereas the π-electron systems present in the cation (four π-electrons) and anion (eight π-electrons) derived from cyclopentadiene and cycloheptatriene, respectively, should not.

The formation of the negatively charged cyclopentadienide ring was first described by Thiele[20] when he prepared potassium cyclopentadienide, and the earliest examples of compounds in which it was recognised that the five-membered ring showed aromatic character were the anhydronium bases[4],[21] such as (XII), in which a negative charge is associated with the five membered ring and a positive charge centred on the nitrogen atom (XIII). Goss and Ingold[22] connected the acidity of cyclopentadiene and its derivatives with the sextet of electrons realised in its anion.

Other early examples of the aromaticity of the negatively charged five-membered ring were the fluorenylides (XIV)[23] and (XV)[24]; investigations of the dipole moments of these molecules confirmed their highly polar character[25],[26]. The first compound to be described with an ylide structure derived from cyclopentadiene itself was diazocyclopentadiene (XVI)[27]; the preparation of triphenylphosphonium cyclopentadienylide (XVII) was subsequently reported[28]. The remarkable stability of these compounds results from the delocalisation of a stable system of six π-electrons over the five-membered ring.

Aromatic stability resulting from the tendency of the cyclopentadiene system to accept an electron and thereby acquire a stable aromatic sextet is further shown in the fulvenes in which the extracyclic double bond contributes to the acquirement of the required number of π-electrons. Of special interest is the dipole moment of fulvene which, surprisingly, is as large as 1.0 D. The existence of a dipole moment of such a magnitude in so simple a structure is a reflection on the great tendency of the cyclopentadienide anion to be formed.

The most striking example of the aromatic character of a negatively charged five-membered ring is shown by the abnormal stability and typically aromatic reactions of dicyclopentadienyl iron[29], or ferrocene, in which all the carbon-hydrogen bonds are equivalent and the two five-membered rings planar and symmetrical.

The stability of all of these compounds is to be traced to the system of six π-electrons delocalised over a five-membered ring, thus constituting a stable aromatic system. This is to be contrasted with the failure to effect condensations with, or to form metal salts of, cycloheptatriene[30]. Only one of the anions has therefore been prepared and its properties are completely in accord with theory.

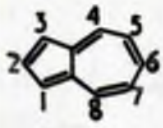
In the positively charged series, cycloheptatrienylium bromide (XVIII), although probably first prepared in 1891[31], has recently been recognised[32] as having a salt-like structure reflecting an amount of delocalisation energy on the cyclic ion large enough to overcome the normal tendency of the carbon-bromine bond to be covalent. Cycloheptatrienone (tropone)(XIX) was first isolated by synthesis in 1951[33], [34] and the alternative name of "cycloheptatrienylium oxide" was suggested as corresponding best to its properties[34]. The ready formation of a stable series of salts of the hydroxycycloheptatrienylium cation (XX) on treatment with acids[33], the abnormally low carbonyl absorption frequency in the infra-red (1633 cm^{-1})[34], the high value of the dipole moment (4.3 D)[35] and the suppression of the chemical reactivity of the carbonyl group, indicate that the molecule is highly polarised in the ground state. This conclusion is supported by the high boiling point of tropone and by the fact that it is soluble in water.

The stability of the cycloheptatrienylium cation is again attributed to the development of a stable system of six π-electrons

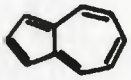
delocalised over the seven-membered ring; in tropone, the complementary negative charge is accommodated on the oxygen atom, as symbolised in (XXI). The instability of the cation derived from cyclopentadiene is indicated by the apparent incapability of cyclopentadienone to exist.

Quantum mechanical theory has predicted that, in addition to the aromatic systems in which stability is attributed to the presence of six π-electrons, a three-membered ring containing two π-electrons should also be aromatic[5], [56]. This prediction would seem to be borne out by the isolation of the stable syn-triphenylcyclopropenyl cation (XXII)[57] but it has not yet been determined how much of the stability is due to the pheryl groups and how much to the cyclopropenyl cation (XXIII), the simplest possible structure which can obey Hückel's rule.

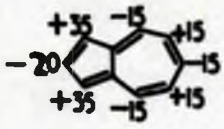
The recent synthesis of diphenylcyclopropenone (XXIV)[58] is of special interest since this is the first known compound containing a carbonyl group in a three-membered ring. Although the greater expected strain in the unsaturated cyclic ketone should seem likely to make it even less stable than cyclopropanone, cyclopropenones should be aromatic, being the analogues in the two π-electron system of tropone in the six π-electron system. The facts that diphenylcyclopropenone can be isolated from a hydroxylic medium and the relatively high temperature (130-140°C) at which decomposition takes place, yielding diphenylacetylene and carbon monoxide, indicates that



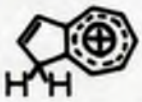
XXVa



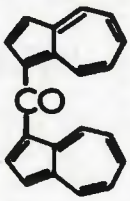
XXVb



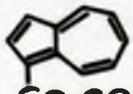
XXVc



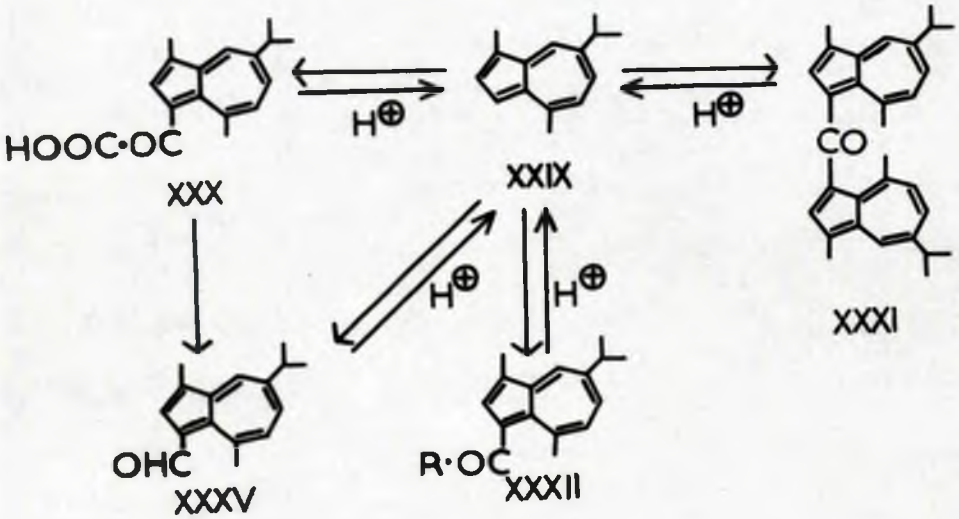
XXVI



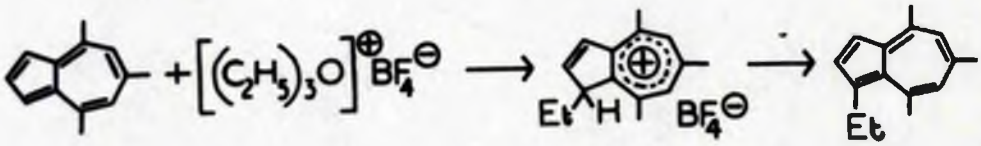
XXVIII



XXVII



XXX XXIX XXXI XXXV XXXII



XXXIII

the cyclopropenone system must have a large resonance stabilisation to compensate for its high angle strain.

The above considerations lead to the most acceptable thermodynamic definition of an aromatic compound as "a cyclic compound with a large resonance energy where all the annular atoms take part in a single conjugated system"[30].

A, I, 2. The Azulene Molecule.

Azulene, or 0:3:5-bicyclodecapentaene, contains fused five and seven membered rings with a system of alternate single and double bonds when it is represented by the classical Kekulé formulae (XXVa and XXVb).

This molecule shows properties to be expected of both a cyclopolyolefin and an aromatic hydrocarbon. The early knowledge of the chemical properties of the azulenes demonstrated their unsaturated character. It was observed (a) that azulenes are readily degraded by oxidising agents, such as nitric acid[40], chromic acid, ozone or potassium permanganate[41] yielding as products acetic acid, acetone and carbon dioxide (b) that vigorous reactions yielding no well-defined products resulted from treatment with bromine or nitrosyl chloride[40] (c) that ready reduction took place either chemically or catalytically

to give products which, in turn, were easily dehydrogenated to the starting material[41] and (d) that azulene could be thermally rearranged to its isomer, naphthalene, complete conversion taking place when azulene is heated at 330° for 24 hours[42]. Mainly as a result of these observations, Pummer[43] concluded that azulene had no aromatic properties.

An important result which emerged from the earlier researches on the azulenes is a generalisation, known as the Plattner Rules,[44],[45] concerning the effect of substituents on the visible absorption spectrum of azulene. Alkylation of azulene produces either a bathochromic or a hypsochromic shift depending on the position, but not on the nature of the alkyl substituent. Thus, in going from azulene to 1-methyl azulene, there is a shift in the visible spectrum of about +36 mμ or -300 cm^{-1}. The displacement shown for each position of the azulene nucleus is given in formula (XXVc). Since the direction and relative magnitude of the shifts are predictable and additive, in the case of the polysubstituted azulenes, the Plattner Rules have been a useful aid in structural studies[46]; determinations of purity can also be carried out by comparing the extinction coefficients of the characteristic visible bands. Only the visible band is abnormal for the ultra-violet absorption undergoes normal translation.

Recent work in the study of azulene has been concerned mainly with the acquisition of a more fundamental knowledge of the properties and chemical behaviour of the molecule. The classical representation as a

resonance hybrid involving structures (XXVa) and (XXVb) indicates that the bridge bond should be incapable of assuming any double bond character and leaves unexplained (a) the blue colour of azulene (b) the fact that azulene has a dipole moment of 1.0 ± 0.05 D[47] (c) the basicity of azulene[48] and (d) the spectra of substituted azulenes.

A study of the spectral properties and the conductivity of a solution of azulene in strong acid led to the conclusion[49] that reversible proton addition to the azulene nucleus takes place. By a subsequent theoretical calculation involving the L.C.A.O. molecular orbital approximation, it was shown[50] that proton addition at position 1 would yield a cation with the greatest resonance energy and would also explain the observed spectral shift in the transformation from azulene. The azulenium cation was therefore formulated as a cyclopentadienocycloheptatrienylium cation (XXVI).

Since protonation may be regarded as the simplest form of electrophilic substitution, it would be expected that substitution by electrophilic reagents generally would occur at position 1. This had earlier been predicted by Brown[51] from calculations of the polarisation energies of the azulene molecule.

In recent years, azulene and its derivatives have been shown to undergo a number of reactions considered expressive of aromatic character. This is illustrated by the following examples.

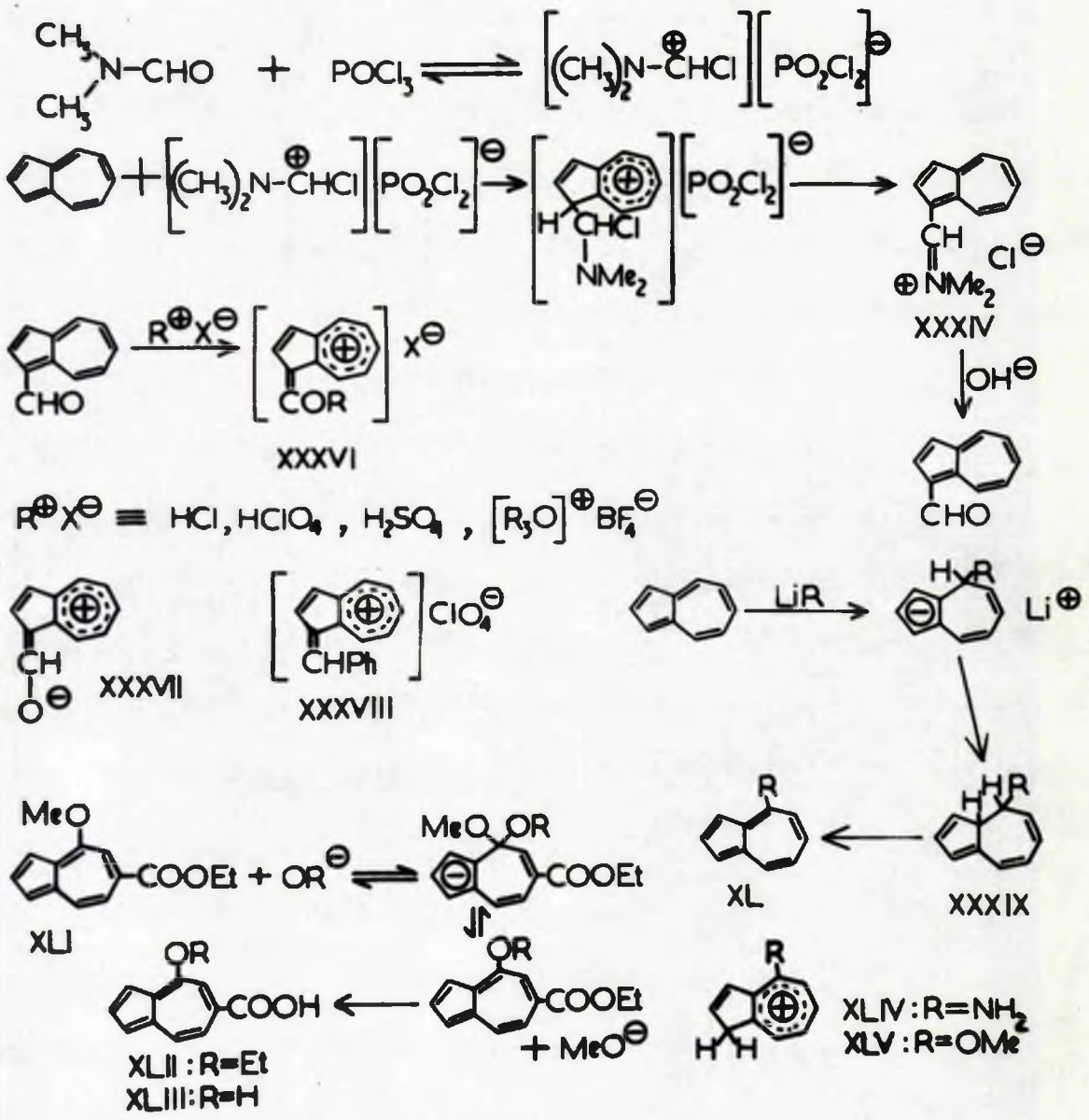
Anderson et al.[52] found that Friedel-Crafts acylation under extremely mild conditions gave, as products, an acetylazulene and a

diacetylazulene. The acetyl substituent in the monosubstituted compound was shown to be in position 1 by conversion to 1-methyl azulenate which has been unambiguously synthesised[53]. This result provided the first experimental confirmation of Brown's prediction.

The entry of acyl substituents has been effected without the aid of catalysts normally required for the corresponding substitution of benzenoid hydrocarbons[54],[55]. Thus, azulene with oxalyl chloride at room temperature forms a mixture of 1-azulenylglyoxalic acid (XXVII) and di-1-azulenyl ketone (XXVIII), the former predominating.

Ease of acylation has also been observed in the guaiazulene molecule (XXIX)[54],[55]. Thus, reaction with oxalyl chloride yields the acid (XXX) and the ketone (XXXI) in comparable amounts, the proportions depending on the nature of the solvent employed. Acetyl bromide with guaiazulene in light petroleum at room temperature affords 3-acetylguaiazulene (XXXII, R=CH_3); when benzoyl bromide and guaiazulene are warmed in the same solvent, 3-benzoylguaiazulene (XXXII; R=Ph) results. 3-Guaiazulenylglyoxalic acid, di-3-guaiazulenyl ketone and 3-acetyl- and 3-benzoylguaiazulene regenerate guaiazulene when treated with strong acids.

1-Nitroazulene was obtained by treatment of azulene with cupric nitrate and acetic anhydride[52], a reaction which has been postulated to proceed via the intermediate acetyl nitrate[56]. By using tetranitromethane in pyridine as nitrating agent and carrying out the reaction at room temperature, a much higher yield of 1-nitroazulene


CH3 N-CHO + POCl3 ⇌ [(CH3)2N-CHCl][PO2Cl2]⊖
XXXIV
XXXVI
R⊕X⊖ ≡ HCl, HClO4, H2SO4, [R3O]⊕BF4⊖
XXXVII
XXXVIII
LiR
Li⊕
XXXIX
XL
XLI
XLII : R=Et
XLIII: R=H
XLIV : R=NH2
XLV : R=OMe

was obtained[37]. This reagent can be used to nitrate benzenoid hydrocarbons only when they are activated by powerful electron releasing substituents, such as hydroxyl and dialkylamino[38]. Tetranitromethane has also been used to nitrate guaiazulene[55].

Friedel-Crafts alkylation of azulene was attempted with a number of reagents and catalysts and under a variety of conditions[39]. Some evidence for the formation of 1-alkyl-azulenes was obtained but only two products, 1-hexyl- and 1-benzylazulene were characterised. Chloromercuration gave a dichloromercuriazulene in high yield[39].

The ethyl group was introduced into position 1 of 4,6,8 trimethyl-azulene by reaction with triethyloxonium fluoroborate followed by hydrolysis of the resultant 1-ethyl-4,6,8-trimethylazulenium fluoroborate (XXXIII)[60]. Azulene on treatment with triphenylmethyl fluoroborate yielded the stable 1-triphenylmethylazulenium fluoroborate which was hydrolysed to 1-triphenylmethyl-azulene[60].

Azulene has been formylated in high yield by reaction with dimethylformamide and phosphorous oxychloride[61],[62]. This reaction is considered to proceed by the attack of a carbonium ion at a site of high electron density, as formulated opposite. The intermediate salt (XXXIV), stabilised by resonance among structures where the positive charge is borne by the seven-membered ring, the extracyclic carbon atom, or the nitrogen atom, can be isolated. 3-Formylguaiazulene (XXXV) results when hydrogen chloride is passed into a suspension of zinc cyanide in an ethereal solution of guaiazulene; it is also

obtained when 3-guaiazulenylglycolic acid (XXX) is heated in aniline at 150° and the resulting Schiff's Base then hydrolysed with dilute hydrochloric acid. Treatment of the molecule with strong acid regenerates guaiazulene.

Azulene-1-aldehyde shows many of the reactions of a typical aromatic aldehyde. Thus, it undergoes oxime formation, reacts with Grignard reagents, condenses with compounds containing an activated methylene group (cyclopentadiene, acetophenone, nitromethane and malonic acid) and is readily reduced by the Wolff-Kishner method or using lithium aluminium hydride. Further, it forms a series of stable salts (XXXVI) with mineral acids. Confirmation that the tropone vinylogue structure (XXXVII) contributes to the structure of azulene-1-aldehyde was obtained by a spectral study of the molecule[63].

When a solution of azulene and an aromatic aldehyde in tetrahydrofuran or glacial acetic acid is treated with 72% perchloric acid, stable salts of type (XXXVIII) can be isolated[64].

The above examples emphasise the high susceptibility of the azulene molecule to attack by electrophilic reagents. By comparison, benzenoid aromatic hydrocarbons in many cases form corresponding derivatives under much more strenuous reaction conditions.

The azulene nucleus is also reactive towards nucleophilic reagents, substitution taking place at position 4 (or 8) as was predicted by Brown[31]. Hafner and Weldes[65] have described the addition of organometallic reagents to the azulene molecule giving a 4-alkyl or

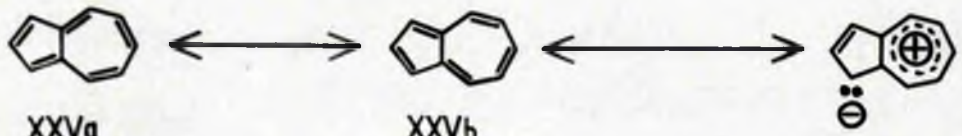
a 4-aryl dihydroazulene (XXXIX). A mild oxidising agent, such as chloranil, is required for the removal of two hydrogen atoms yielding the substituted azulene (XL). Repetition of the process yields a 4:8-disubstituted azulene.

Ready replacement of the methoxy group from ethyl 4-methoxyazulene-8-carboxylate (XLI) took place on boiling the ester with ethanolic or aqueous potassium hydroxide solution giving, respectively, 4-ethoxy- and 4-hydroxyazulene carboxylic acid (XLII) and (XLIII). Amination of azulene was observed to take place in position 4[46]. Preferential protonation of carbon took place in 4-amino- and 4-methoxyazulene, giving a substituted amino- or methoxy- cycloheptatrienylium cation (XLIV and XLV or isomers).

Azulene, therefore, can be classified as aromatic with respect to the facts that (i) it readily forms molecular complexes[48] (ii) it is formed in dehydrogenation reactions[41] (iii) the azulene molecule has a resonance energy of 46 K cal/mole[66], [67] and (iv) it is readily substituted by electrophilic and nucleophilic reagents.

The low value of the dipole moment[47] shows that polarisation of the ground state does not occur to a significant extent. Anderson[52] considered the electrophilic substitution and resonance stabilisation of azulene from a simplified molecular-orbital standpoint and represented the ground state of the molecule as a resonance hybrid of the two classical Kekule structures (XLVa) and (XLVb) with a small contribution from dipolar forms of the type (XLVI). The

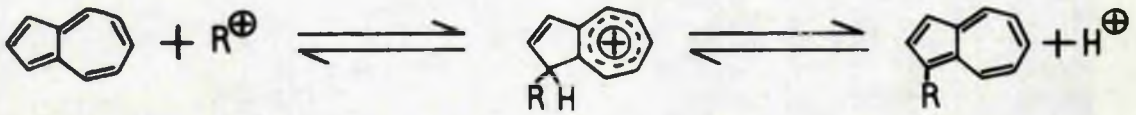
The ground state of azulene:



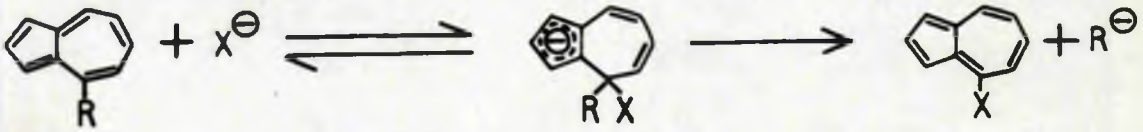
XXVa XXVb XLVI

Substitution of the azulene nucleus:

1. Electrophilic substitution:



2. Nucleophilic substitution:



R=H or substituent

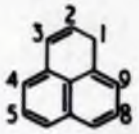
thermodynamic stability[47],[67] of the molecule is attributed to a ring of ten overlapping 2p π-atomic orbitals disposed essentially round the periphery of the molecule.

This representation of the ground state means, then, that in azulene aromatic character is invested inthe delocalisation of ten π-electrons over a carbocyclic structure, formally bicyclic through essentially monocyclic with respect to the π-electron system. In the ground state, the transannular bond contributes nothing to the aromatic character; however, it enables the molecule to retain a planar structure so that π-electron delocalisation becomes possible and effective. This formulation is in complete agreement with Huckel's rule that aromatic character will be shown in closed conjugated planar structures containing $(4n + 2)$ π-electrons; further, the cyclo-decapentaene structure containing a transannular valency bridge is borne out by the reactions in which azulene shows polyolefinic character, notably its instability towards oxidising and reducing agents.

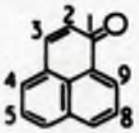
The behaviour of azulene in reactions indicative of aromatic character shows that it is during reaction that importance must be attached to the stability of π-electron sextets associated with the five- and seven-membered ring. Electrophilic attack is accompanied by the formation, in the transition state, of a substituted cyclopentenotropylium cation. During nucleophilic attack, transition-state stability arises from the development of a stable

sextet in the five membered ring. The transannular bond also plays an important part during reaction for it permits the development of a stable π-electron system in the transition state; thus, the transition-state energy is favourably low and reaction facilitated.

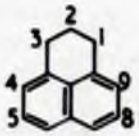
It is therefore this easy transformation from one stable system in the ground state to another in the transition state which explains the mild conditions under which azulene undergoes aromatic electrophilic and nucleophilic substitution reactions.



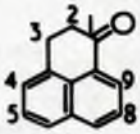
XLVII



XLVIII

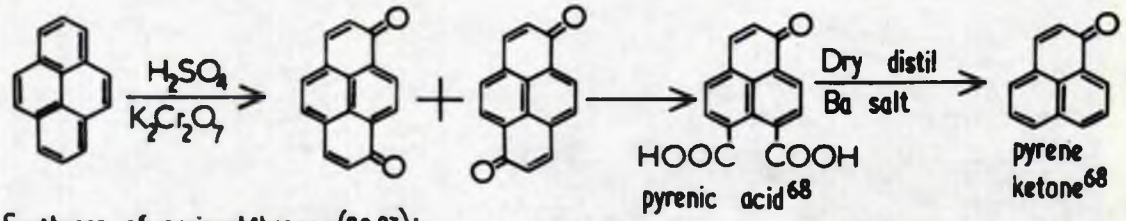


XLIX

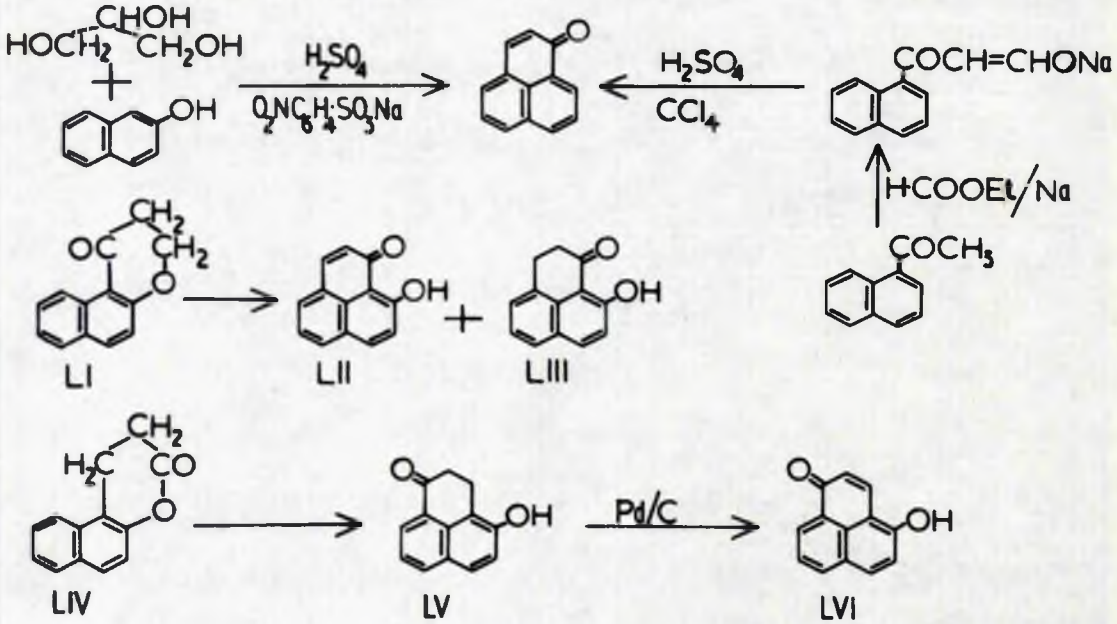


L

The degradation of pyrene[71]:-



Syntheses of perinaphthenone (80,83):-



A.II. The Perinaphthene Ring System.

A. II. i. Nomenclature.

Prior to 1936, three systems of naming the tricyclic compounds (XLVII) to (L) were employed, none of which was strictly accurate in its implications.

The ketone (XLVIII) was referred to as pyrene ketone[68], phenalone-9[69],[70], 1,8-naphthindenone[71], 9-ketoperinaphthindene[72], and perinaphthindone[73],[74], and for the parent hydrocarbon (XLVII), the following names had been suggested:-

(i) perinaphthindene[75],[76]

(ii) phenalene (= phenonaphthalene)[69]

(iii) benznaphthene (= peribenzonaphthalene)[77], a name which implies complete conjugation, which the hydrocarbon does not possess.

Fieser and Hershberg[78] suggested a more uniform system of nomenclature, the compounds (XLVIII), (XLIX) and (L) being named perinaphthenone, perinaphthene and perinaphthen-1-one, respectively and, in accord with this nomenclature, compound (XLVII) was named as perinaphthene. The numbering employed is as illustrated in formulae (XLVII) to (L) and is based on the ring index system. Thus perinaphthene (XLIX) ≡ 2,3-dihydroperinaphthene and perinaphthen-1-one (L) ≡ 2,3-dihydroperinaphthenone.

A, II, 2. Preparations of Perinaphthenones.

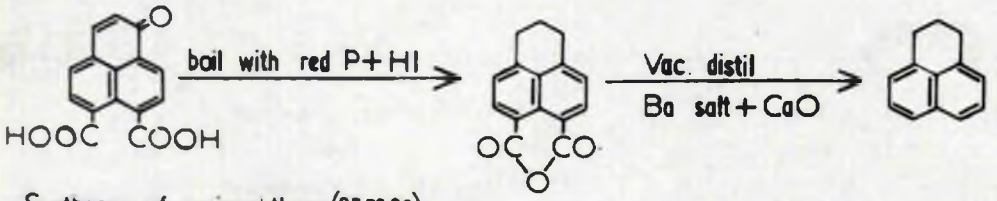
The first recorded evidence that a derivative of perinaphthene was known appeared in a paper by Bamberger and Philip[68] who isolated "pyrene ketone" by the oxidative degradation of pyrene. It was later shown[71] that the oxidation proceeds to give a mixture of pyrene quinones, each of which on further oxidation yields the same perinaphthenone dicarboxylic acid. Bamberger and Philip made one important observation, namely, that perinaphthenone is basic and dissolves immediately in concentrated hydrochloric acid, from which solution it can be obtained on dilution.

The synthesis of a yellow substance (m.pt. 152°), considered to be the ketone (XLVIII), is described in the early patent literature[70]. This compound was obtained by heating either α- or β-naphthol with glycerol and 82% sulphuric acid, the acid presumably functioning as a dehydrating, condensing and oxidising agent. Cook and Hewett[70] noted that the reported properties were similar to those of the "pyrene ketone" (m.pt. 142°) of Bamberger and Philip and also to those of the product (m.pt. 153-154°) formed with other substances from β-(1-naphthyl)- propionic acid under the cyclising and dehydrogenating influence of stannic chloride[70], or of aluminium chloride acting on the acid chloride[69]. Vollman et al.[71] made a direct comparison of the material prepared according to the patent with a purified sample of "pyrene ketone" (m.pt. 152°) and found the two to be identical. A later patent[80] included a detailed description of an

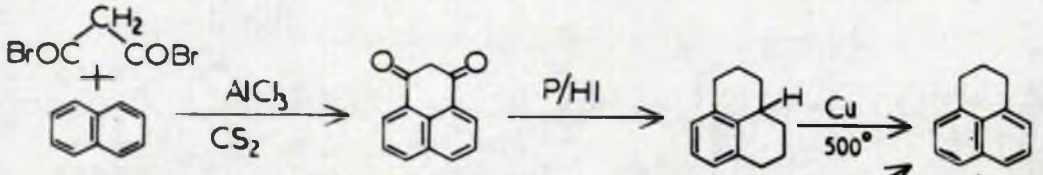
improved procedure in which sodium nitrobenzene sulphonate was used as the oxidising agent and this procedure has been employed with success as a means of preparing perinaphthenone in quantity in 26% yield from β-naphthol[75],[78],[81]. Anhydrous hydrogen fluoride has also been used as the condensing agent in the preparation of perinaphthenone from α- or β- naphthol and acrolein[87]. A synthesis utilising the condensation of α-acetylnaphthalene with ethyl formate, followed by cyclisation of the resulting oxymethylene compound with 82% sulphuric acid, has been described[85]. Purified perinaphthenone melts at 156-156.5°C.

Details are given in the patent literature for the preparation of a number of substituted perinaphthenones[84]. An interesting route to the hydroxyperinaphthenones was described by Loudon and Razdan[83]. 3,6-Benzchrysen-4-one (LI) was converted by fusion with aluminium chloride to a mixture of 9-hydroxyperinaphthenone (LII) and 8-hydroxyperinaphthenone (LIII); 4-hydroxyperinaphthenone (LVI) was prepared from 3,4-dihydro-4,5-benzocoumarin (LIV) after dehydrogenation of 4-hydroxyperinaphthenone (LV), the primary product of aluminium chloride fusion.

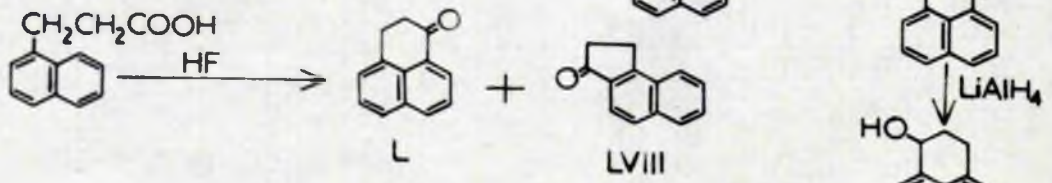
Isolation of perinaphthane(86):—



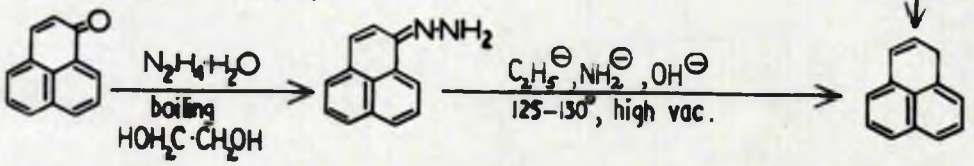
Syntheses of perinaphthane(87,78,89):—



Synthesis of perinaphthanone(88):—



Syntheses of perinaphthene(83,105):—



A. II. 3. Preparations of Perinaphthane.

Perinaphthane (XLIX) was first isolated by Langstein[66] who obtained a small amount of the crystalline hydrocarbon by the reduction of pyrenic acid, a product of the oxidative degradation of pyrene. A synthesis was accomplished by Fleischer and Retze[67] from naphthalene and malonyl bromide but the process involved reduction of the resulting diketone with red phosphorus and hydrogen iodide at 150-180°, followed by dehydrogenation of the over-reduced product over copper at 300°. The method was thus hardly practical for preparative purposes and the first satisfactory method for preparing perinaphthane in quantity was described by Fieser and Hershberg[78] who obtained the hydrocarbon in 70% yield from perinaphthenone by hydrogenation in dioxane or ether at high pressure in the presence of a copper chromite catalyst at 250-300°. After the discovery of a satisfactory method for the preparation of perinaphthan-1-one in quantity[88], an improved method for the preparation of perinaphthane by catalytic hydrogenation of perinaphthenone was described[89]. A number of alkylated perinaphthenes have been prepared by the Clemmensen-Martin reduction of the corresponding perinaphthenones[90]-[97]. The parent hydrocarbon has also been prepared by the hydrogenation of perinaphthene[85].

A. II. 4. Preparation of Perinaphthen-1-one.

In the early preparations of what was regarded as being essentially perinaphthen-1-one (L) the purity and identity of the product was suspect and some confusion existed concerning the characterisation of the acid from which the ketonic material was prepared by cyclisation. Thus the following melting points were reported for the amide of β -(1-naphthyl-)- propionic acid (LVII): 140°(98), 85° (69), 135°(99), although investigators seemed agreed as to the melting point of the acid obtained by the malonic ester synthesis from α-chloro or α-bromo-methylnaphthalene. Mayer and Sieglitz(99) cyclised β-(1-naphthyl-)propionic acid chloride using aluminium chloride in ligroin and obtained in poor yield a yellow ketonic substance melting at about 85-86°C and considered to be perinaphthen-1-one. von Braun et al.(100) investigated this preparation and concluded that it was necessary to use ligroin or carbon disulphide as a solvent for cyclisation. In nitrobenzene, perinaphthenone was formed in 50% yield. Cook and Hewett(70) also repeated the cyclisation described by Mayer and Sieglitz and found that material obtained in this way was a mixture and that the yellow colour was due to the presence of a significant amount of the dehydrogenation product, perinaphthenone (XLVIII), which they isolated and identified. On heating the acid (LVII) with stannic chloride, they obtained the same substance along with a small amount of a saturated ketone, m.pt. 120-121°C, evidently corresponding to one of the alternative

structures (L) and (LVIII). Darzens and Lévy[99] conducted the cyclisation of (LVII) by the Friedel-Crafts procedure in nitrobenzene and obtained in good yield a yellow substance melting at 86°C.

Similar anomalies exist in the literature on the products of the cyclisation of a number of substituted naphthyl propionic acids. Thus, Berger and Starling[101] reported that the cyclisation of β-(2-methoxy-1-naphthyl)- propionic acid using phosphorus pentoxide in benzene yielded 4-methoxyperinaphthan-1-one. It was later shown[102] that the product was a mixture of unsubstituted perinaphthenone and 4-methoxyperinaphthenone and that the substituted perinaphthan-1-one was best prepared by the use of anhydrous hydrofluoric acid, or stannic chloride in benzene, to cyclise the propionic acid, in which cases there was no evidence for the formation of a perinaphthenone derivative.

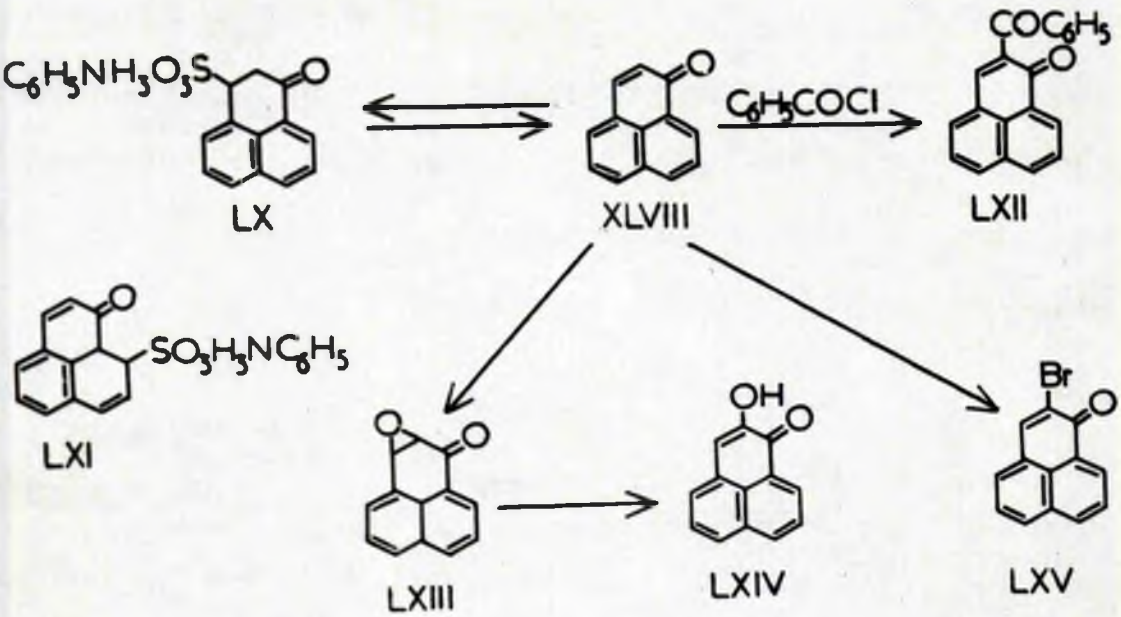
Fieser and Cates[88] showed that the interfering dehydrogenation reaction in the cyclisation of β-(1-naphthyl) propionic acid can be avoided almost completely by using anhydrous liquid hydrogen fluoride to effect the ring closure. The main product was obtained in 81% yield and was identified as perinaphthan-1-one (L) by Clemmensen reduction to the known perinaphthene[78]. The purified, colourless ketone melts at 82.6-83.2° The higher melting, yellow preparations of the earlier workers[89],[99], while evidently impure, gave oximes corresponding fairly closely in melting point to the oxime obtained by Fieser and Cates, showing that in all cases substantial amounts

of perinaphthan-1-one had been formed although isolated in amounts depending on the extent of secondary dehydrogenation to perinaphthenone by the catalyst. The by-product from the hydrogen fluoride cyclisation of the acid (LVII), isolated by Fieser and Gates in 6% yield as colourless needles melting at 120-121°, showed a close correspondence in melting point and in the melting point of the oxime, with Cook and Hewett's ketone and was therefore assigned the structure of the product of β-cyclisation, 4,5-benzhydrindone-1 (LVIII).

The method of Fieser and Gates is the only satisfactory one for the preparation of pure perinaphthan-1-one in quantity.

A. II. 5. Preparation of Perinaphthene.

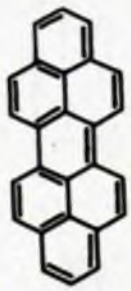
Although a number of attempts had previously been made to prepare the parent hydrocarbon, perinaphthene (XLVII)[21][103][104], it was not until 1944 that the compound was first isolated. Look and Gergely[83] formed the hydrazone of perinaphthenone by treating the ketone with hydrazine hydrate in boiling glycol. It was isolated as brown-yellow needles, melting at 125-130°C, and on heating in a high vacuum at 125-130°C in the presence of ethoxy, amide or hydroxyl ions, perinaphthene was obtained in poor yield as colourless plates, unstable in air, and characterised by reduction to perinaphthene and by oxidation



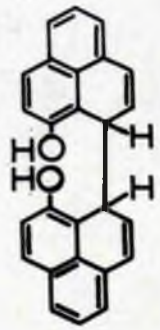
LX XLVIII LXII

LXI

LXIII LXIV LXV



LXVI



LXVII

(atmospheric oxygen or chromic anhydride) to perinaphthenone. More recently, Bankalkaids and Lerrabee[105] have shown that perinaphthene can conveniently be prepared on a practical scale by the dehydration of perinaphthan-1-ol (LXX) using ethanolic hydrogen chloride. Although other methods of dehydrating perinaphthanol have been attempted without success[81], this procedure gives perinaphthene in yields of 85 to 88% and represents the best method for the preparation of the hydrocarbon. Perinaphthanol is prepared by the lithium aluminium hydride reduction of perinaphthan-1-one.

A. II. 6. The Properties of Perinaphthenone.

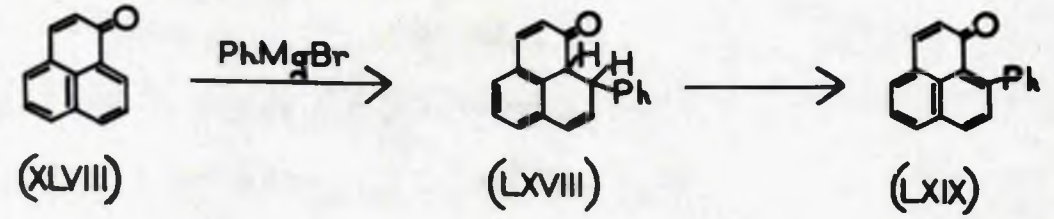
The properties of the carbonyl group in perinaphthenone and substituted perinaphthenones are rather abnormal.

Like an unsubstituted quinone, perinaphthenone reacts with sodium bisulphite to give a colourless addition product which was isolated in the form of an aniline salt presumed to have the structure (LX)[81]; however, it is possible that, by analogy with the addition of Grignard reagents, addition takes place at position 9 yielding a salt having the structure (LXI). Treatment of the salt with dilute hydrochloric acid at the boiling point reverses the reaction and precipitates the ketone (XLVIII). It has been reported that perinaphthenone yields no phenylhydrazone and with hydroxylamine it

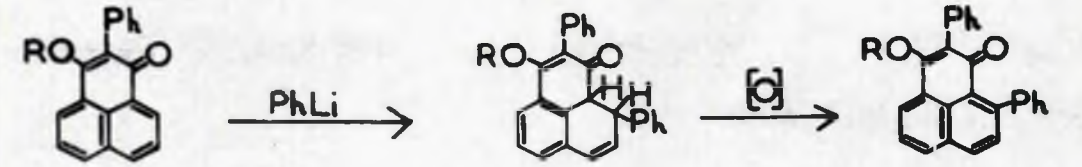
forms a compound of unknown structure containing no nitrogen[73]. However, Fieser and Newton[81] found that the expected oxime can be obtained by boiling the ketone under reflux with hydroxylamine hydrochloride in ethanol and Lock and Gergely[85] formed the hydrazone by boiling the ketone under reflux with hydrazine hydrate in glycol.

Attempts to utilise perinaphthenone as a component in the Michael reaction, the Diels-Alder reaction, or the Friedel-Crafts condensation with benzene in the presence of aluminium chloride, were unsuccessful and usually resulted in the recovery of starting material[81]. Under forcing conditions, however, a Friedel-Crafts condensation with benzyl chloride took place yielding 2-benzylperinaphthenone (LXII). In the reaction with hydrogen peroxide in aqueous alcohol, perinaphthenone was found to be attacked much less readily than 2-methyl-1,4-naphthoquinone[106], but, after prolonged heating, the substance was converted to the epoxide (LXIII). The isomerisation of this substance was effected, as in the naphthoquinone series[107], with concentrated sulphuric acid[81] yielding 2-hydroxyperinaphthenone (LXIV) as a red alkali-soluble substance melting at 185°C. Evidence for the structure of this compound came from the fact that its properties were different from those of the known 3-hydroxy-perinaphthenone[108], the other possible isomerisation product.

Perinaphthenone has been halogenated[100]-[114] but the reactions are complicated and proceed through several stages[115]. Attempts



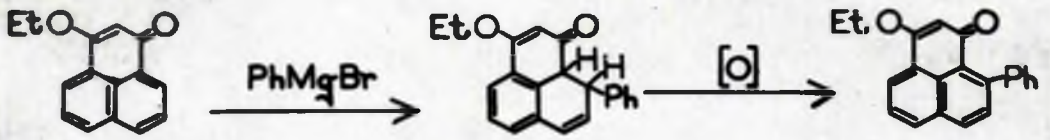
(XLVIII) (LXVIII) (LXIX)



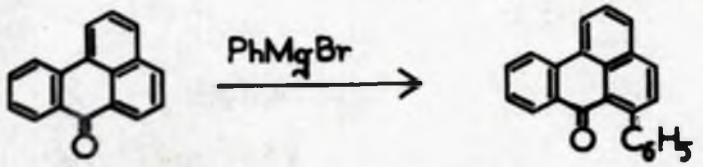
(LXX: R=H)
(LXXI: R=CH_3)

(LXXII: R=H)
(LXXIII: R=CH_3)

(LXXIV: R=H)
(LXXV: R=CH_3)



(LXXVI) (LXXVII) (LXXVIII)



(LXXIX) (LXXX)

Abnormal carbonyl reactions in the perinaphthenone series

to convert 2-bromoperinaphthenone (LXV) to the hydroxy compound (LXIV) were unsuccessful, the substance being recovered unchanged after treatment with silver acetate under forcing conditions[81].

Peropyrene (LXVI) and perinaphthene are the products when perinaphthenone is heated with zinc dust in a melt of sodium chloride and zinc chloride[116]. It was suggested that a bimolecular reduction product (LXVII) is first produced which undergoes spontaneous intra-molecular dehydration.

In reactions with organo-metallic compounds, perinaphthenone and its derivatives do not yield the expected products. Phenyl magnesium bromide reacts with perinaphthenone yielding 9-phenyl-perinaphthenone (LXIX) after distillation of the intermediate (LXVIII)[117]. The structure of (LXIX) was proved by oxidation to the known 2-phenyl-naphthalic anhydride.

1,4 Addition of organo-metallic reagents to the perinaphthenone skeleton has also been observed in the following cases:

a) Phenyl lithium reacts with 2 phenyl 3 hydroxy perinaphthenone (LXX) and with its methyl ether (LXXI) yielding, after oxidation, 2,9-diphenyl- 3-hydroxy-perinaphthenone (LXXIV) and 2,9-diphenyl-3-methoxy-perinaphthenone (LXXV), respectively[118]. The primary addition products (LXXII) and (LXXIII) were isolated.

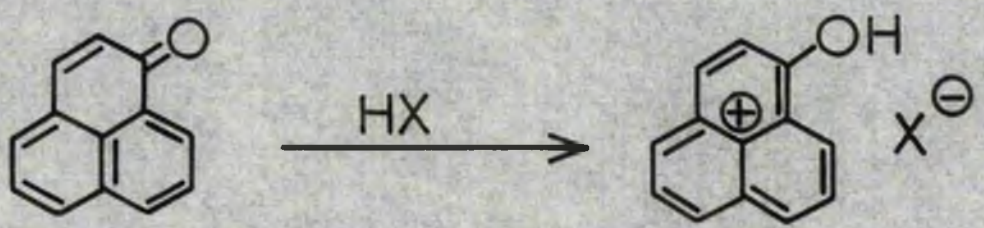
b) Phenyl magnesium bromide adds 1,4 to 3-ethoxy-perinaphthenone (LXXVI) yielding the intermediate (LXXVII) which on oxidation gives 3-ethoxy-9-phenyl-perinaphthenone (LXXVIII)[119] the structure of which

was proved by hydrolysis followed by oxidation to 2-phenylnaphthalic anhydride.

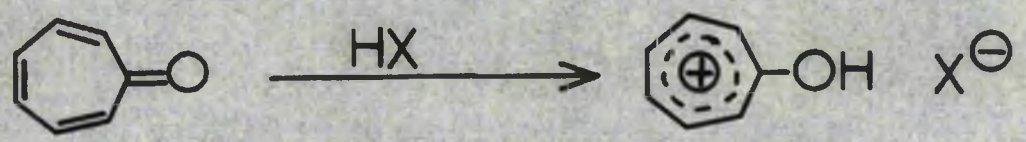
e) Benzanthrone (LXXIX) reacts with phenyl magnesium bromide to yield 4-phenylbenzanthrone (LXXX)[120].

d) o-Tolucylmagnesium bromide, α-2-methylnaphthyl magnesium bromide and mesityl magnesium bromide likewise undergo 1,4-addition to perinaphthenones[121] with formation of the corresponding 9-aryl-perinaphthenone.

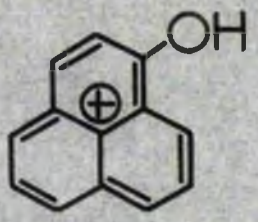
The most significant property of perinaphthenone is its reversible solubility in concentrated acid. This abnormally high basicity of the ketone is of considerable value in the separation of perinaphthenones from other ketones and non-basic material and has been observed and commented on by several workers[68],[70]. It means either (a) the carbonyl group is abnormally polarised with unusually high electron density on the oxygen atom conferring great basicity on the ketone or (b) the carbon-oxygen bond is capable of an unusually ready polarisation. Perinaphthenone, therefore, shows an obvious analogy with tropone (XIX), both ketones forming a stable series of salts (LXXXI) and (XX) on treatment with acids.



(XLVIII) (LXXXI)



(XIX) (XX)

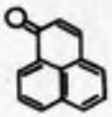
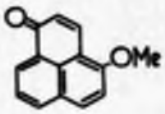
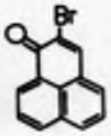
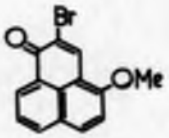
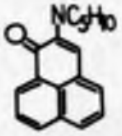
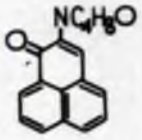
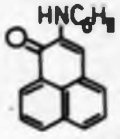
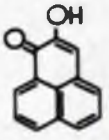
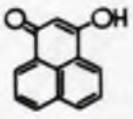


(LXXXII)

Thus, a sulphate has been obtained from perinaphthenone and 68% sulphuric acid dissolved in excess acetic acid and, likewise, a nitrate of variable composition by direct treatment of the ketone with nitric acid. A hydrochloride and a hydrobromide have been prepared by passing the appropriate hydrogen halide into a benzene solution of the ketone. All the above salts are yellow crystalline solids with characteristic melting points but the halides appear to evolve hydrogen halide slowly on standing and are readily hydrolysed by water[132].

The dissociation constant (pKa) for the conjugate acid (LXXXII) of perinaphthenone, as well as that for the conjugate acids of benzanthrone and benzalacetophenone, has been determined by a method involving the spectrophotometric estimation of the partition of the appropriate ketone between an acid and an immiscible organic solvent mixture[125]. It was concluded from the results obtained that perinaphthenone is more readily protonated than the other ketones.

The ultra-violet and infra-red spectral bands have been described and discussed for a number of substituted perinaphthenones and

	WAVE NUMBER CM^{-1}	REFERENCE
	1637	126
	1632	125
	1640	127
	1628	125
	1630 1619	124
	1637 1621	124
	1632 1615	124
	1630 1618	127 C,IX,10
	1626	127

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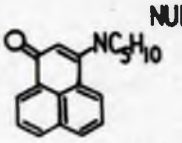
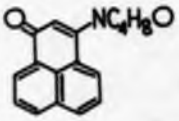
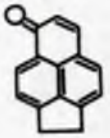
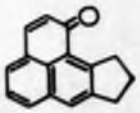
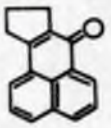
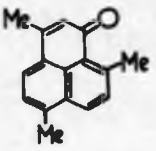
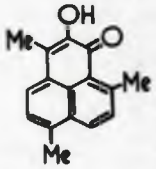
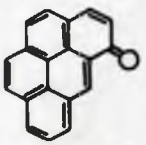
	1633 1611	124
	1633 1611	124
	1634 1618	128
	1637 1621	129
	1634	C,I,5
	1639	C,XIII,3
	1608	C,IX,9
	1639	C,VIII,2

TABLE I. Carbonyl stretching frequencies in the perinaphthenone series

perinaphthanones[124]-[127]. The spectral properties of the perinaphthenones confirm the view that the molecules are polarised to an abnormally great degree in the ground state.

Perinaphthenone shows evidence in the ultra-violet and infra-red regions of extensive resonance interaction between the carbonyl group and the rest of the molecule but this resonance stabilisation is decreased in the dihydro derivative as is evident from the decreased intensity and hypsochromic shift (380-430 Å) of the absorption band in the 3000-4000 Å region[127]. In the infra red, the carbonyl absorption frequency is unusually low (1657 cm^{-1})[126], indicating considerable polarity of the carbonyl group. This is in keeping with the abnormal basicity of the ketone and it is, indeed, a characteristic property of substances containing the perinaphthenone nucleus (Table 1). Introduction of substituents into the α-position results in shifts of the carbonyl stretching frequency to lower wave numbers indicating a more polar carbonyl group.

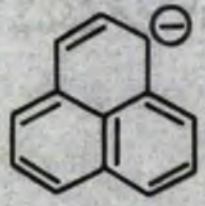
A, II, 7. The Properties of Perinaphthene.

Owing to difficulties in the early attempts to prepare perinaphthene, it was not until 1950 that a study of the properties of the molecule was instigated by Boekelheide and Larrabee[105] who

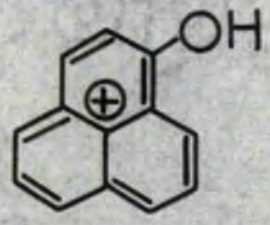
prepared perinaphthene in good yield.

Perinaphthene forms colourless plates melting at 85-86°C and is unstable in contact with air, discolouring in a matter of hours and becoming completely black within a few days. It is reduced catalytically to perinaphthane[83] and can be readily oxidised, either by means of atmospheric oxygen[83] or by using sodium dichromate in glacial acetic acid[105], yielding perinaphthenone.

Perinaphthene readily forms a lithium salt on treatment with phenyllithium in ether solution and was found by exchange reactions to be more acidic than triphenylmethane and less acidic than cyclopentadiene.

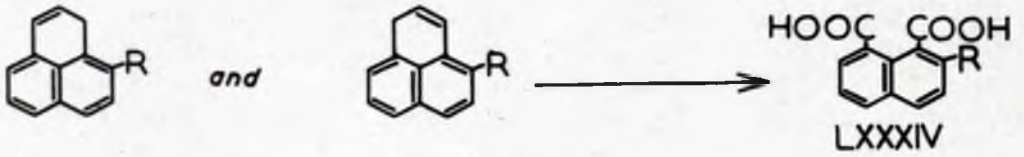


(LXXXIII)

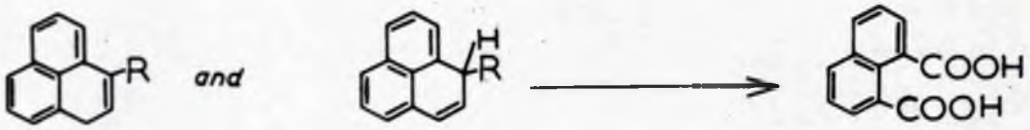


(LXXXIII)

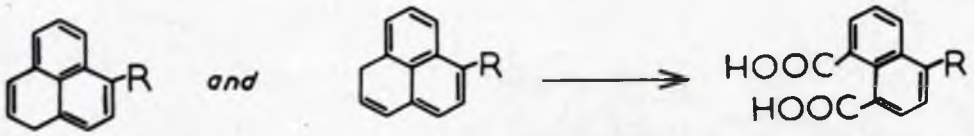
Bockelheide and Larrabee considered that the interesting properties of the molecule are caused by the high degree of resonance stabilisation in the symmetrical mesomeric ions to which it can give rise e.g. the anion (LXXXIII and resonance forms) has a highly stabilised negative charge; also, the solubility of perinaphthenone



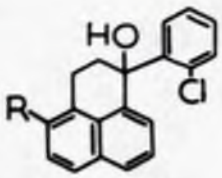
LXXXIV



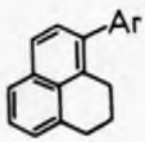
LXXXV



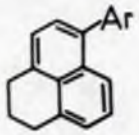
LXXXVI



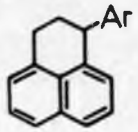
LXXXVII : R=H
XCI : R=OMe



LXXXVIII

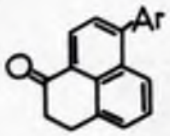


LXXXIX

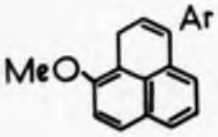


XC

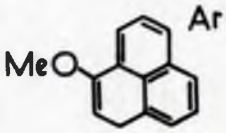
Ar ≡ o-C_6H_4CN



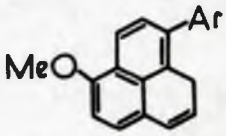
XCII



XCIII



XCIV



XCV

Ar ≡ o-C_6H_4Cl

in concentrated acids to give yellow solutions[70] is caused by resonance stabilisation of the cation (LXXXII and resonance forms). Mobility of a proton in such systems is supported by some results which will be outlined in the following section.

A. II. 8. Isomerisation in the Perinaphthene Series.

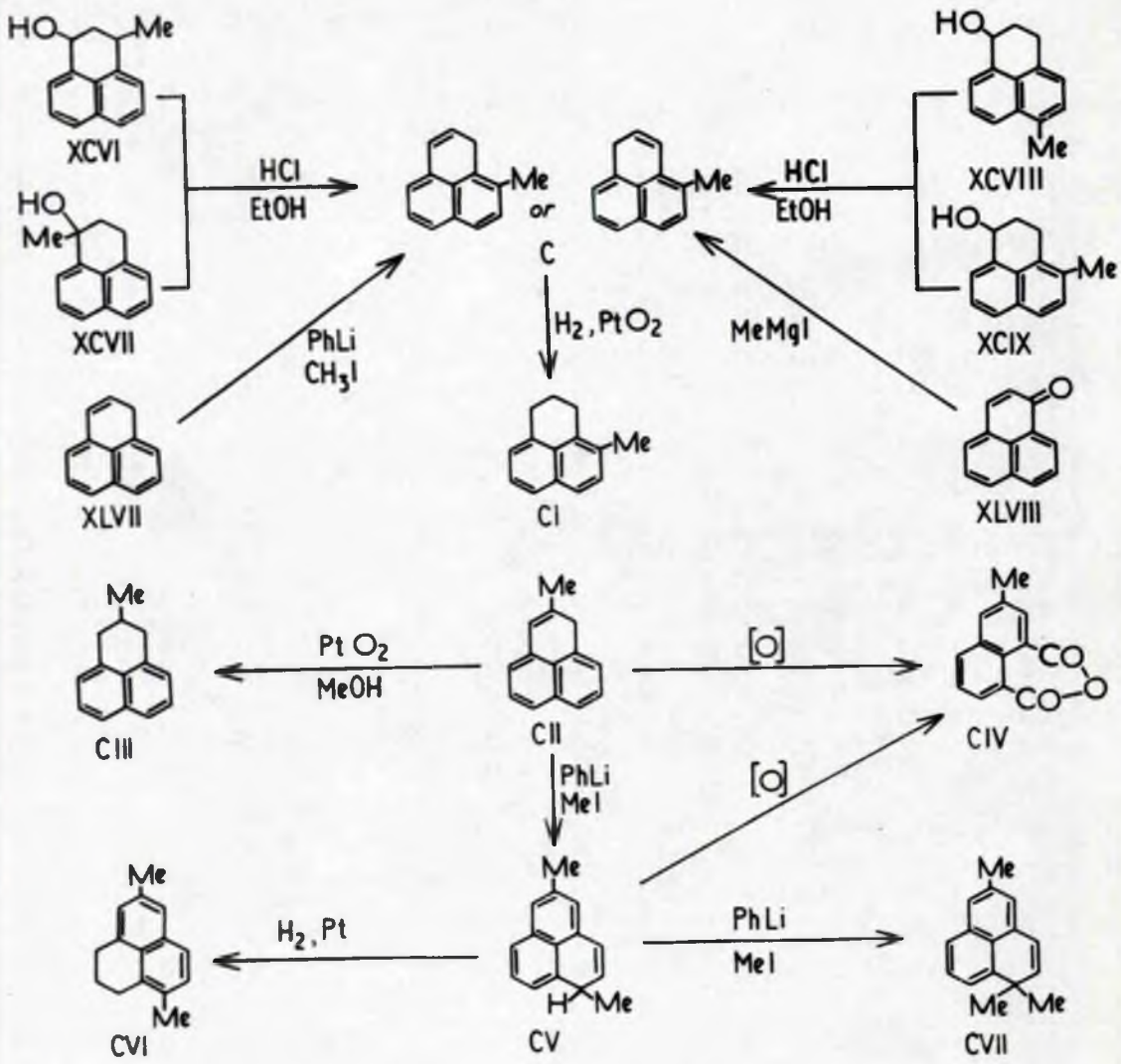
In view of the symmetry of the perinaphthene structure, Klyne and Robinson[130] suggested that, by analogy with the two tautomerides of an unsymmetrical indene, an alkylperinaphthene might exist in six forms, each of the three six-membered rings assuming the aromatic and the unsaturated character in turn. Oxidation would then lead, in the event of the occurrence of six-fold tautomerism, to a mixture of three dicarboxylic acids of a naphthalene derivative (LXXXIV), (LXXXV) and (LXXXVI).

Klyne and Robinson were, however, unsuccessful in their attempts to prepare 9-methylperinaphthene and 8,9-dimethylperinaphthene and did not attain their objective in demonstrating prototropy in the perinaphthene series.

However, the double bond mobility which is inherent in the

conception of Klyne and Robinson was demonstrated by the results of some later workers. Fieser and Gates[88] showed that when the carbinol (LXXXVII), resulting from the reaction of perinaphthenone with o-chlorophenyl magnesium bromide, was submitted to a series of reactions involving dehydration, reduction, and replacement of chlorine by a cyano group, without isolation of the intermediates, two products were obtained which were shown to have structures (LXXXVIII) and (LXXXIX). It was suggested that these products must have arisen by a bond migration in the initial product of dehydration and, as there was no evidence of formation of the normal product (XC), unaccompanied by bond migration, the driving force in the rearrangement is the tendency to conjugation between the chlorophenyl group and a naphthalene system. However, since the intermediate perinaphthene was not isolated and since the results can also be interpreted on the basis that the Grignard addition occurred in both a 1,4 and a 1,6 fashion, isomerisation was not definitely established.

A similar rearrangement, which frustrated an attempt to synthesise 10-methoxy-5:4-benzpyrene, was observed by Badger, Carruthers and Cook[103]. By reaction of 4-methoxyperinaphthen-1-one with o-chlorophenylmagnesium bromide, the carbinol (XCI) was obtained. This carbinol, on treatment with a little iodine in boiling petrol or with cold, dilute methanolic HCl, underwent not only dehydration but also rearrangement and demethylation to yield the ketone (XCII) as sole product. The formation of such a ketone may be interpreted



Isomerisation of the methylperinaphthenes.

as the result of dehydration of the carbinol (XCI) to (XCIII), followed by rearrangement to (XCIV). (XCIV) would be the enol of an ether and its hydrolysis and conversion to (XCII) under the experimental conditions used would not be surprising. It is of considerable interest that the ketone (XCII) was the only product formed, and that it was not accompanied by compounds of type (XCV) structurally analagous to an intermediate leading to one of the compounds (LXXXVIII) isolated in the work of Fieser and Gates[88]. This result supports the conception of Klyne and Robinson of the tautomeric character of the perinaphthene system for if (XCIV) and (XCV), for example, are regarded as being in tautomeric equilibrium, then the equilibrium would be disturbed by conversion of (XCIV) to the ketone (XCII) so that ultimately (XCV) would be wholly converted into (XCII).

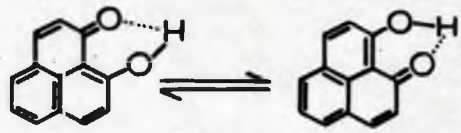
Evidence of tautomerism in the alkyl-perinaphthenes was provided by the work of Dockelheide and his associates[131],[132]. When the alcohols (XCVI) - (XCIX) were dehydrated with a view to obtaining a series of monomethylperinaphthenes having the methyl group located at the 1,5,7 and 9 positions, respectively, it was discovered that all of these preparations led to the same hydrocarbon which from its behaviour on catalytic hydrogenation, was assigned the structure of 4-(or 9) - methylperinaphthene (C)[131], the position of the peri double bond remaining uncertain. Two other experiments were carried out which also demonstrated the singular ease with which (C) is formed in preference to the other possible isomers. Alkylation of

perinaphthene (XLVII) with phenyl lithium and methyl iodide yielded (C) in 85% yield[105]. Since the initial product of this reaction must be 1-methyl perinaphthene, isomerisation occurred even although no acid was present and no temperature higher than that of refluxing ether was attained. Secondly, the reaction of methyl magnesium iodide with perinaphthenone (XLVIII) which had been reported[105] to yield a methylperinaphthene, was repeated by Boekelheide and Larrabee[131] and found to yield (C). Catalytic hydrogenation of (C) yielded 4-methylperinaphthene (CI), isolated as its trinitrobenzene complex.

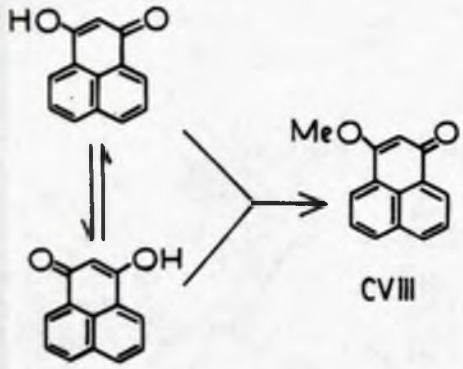
In the series of monomethylperinaphthenes where the positions possible for the methyl group are 2-, 3- and 6, 2-methylperinaphthene (CII) appeared to be the most stable member as catalytic reduction yielded 2-methylperinaphthene (CIII). However, oxidation of (CII) with permanganate in acetone yielded not the expected naphthalic anhydride but instead, 3-methyl-naphthalic anhydride (CIV). This result emphasises again the ease of tautomerism in these systems and in the case of the hydrocarbon (CII) it appears that oxidation and reduction preferentially attack different tautomers.

The methylation of 2-methylperinaphthene (CII) was studied and was found to yield a dimethyl- and a trimethyl-perinaphthene[152]. Synthetic and degradative studies established that the dimethyl-perinaphthene was (CV), with the second methyl group in position 6 with respect to 2-methylperinaphthene. In (CV), oxidation and reduction were again found to attack different tautomers, oxidation

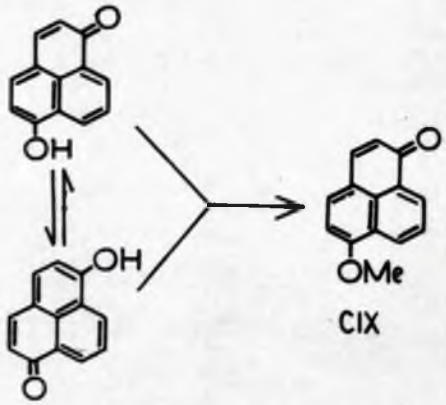
LVI



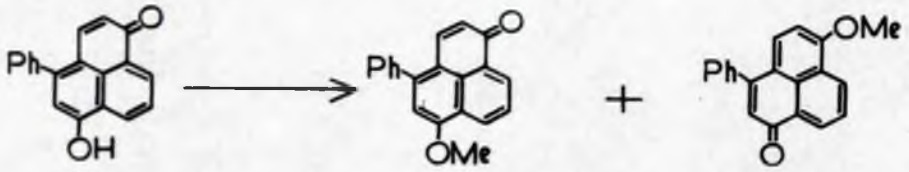
LII



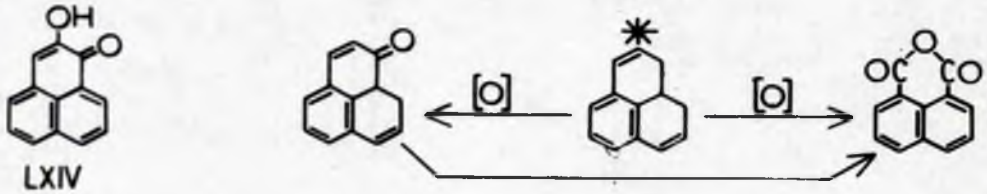
CVIII



CIX



CX CXI CXII



LXIV

yielding 2-methyl-naphthalic anhydride (CIV) and reduction yielding 4,8-dimethylperinaphthane (CVI). On treatment with phenyl lithium and methyl iodide, (CV) yielded a trimethylperinaphthene; attempts to obtain further methylation products failed, presumed by Boekelheide and Goldman to be due to the formation of a gem dimethyl grouping in the trimethyl derivative, which was therefore formulated as (CVII).

The tautomeric properties of the perinaphthene ring are further evident in the properties of the hydroxyperinaphthenones. Depending on the position taken by the hydroxyl group, these compounds can be divided into three classes as follows:

(i) 4-(or 7)-Hydroxyperinaphthenone (LVI)[85],[155] which, because of its tautomeric properties, afforded two methyl ethers, identified by oxidation to 2- and 4-methoxy-naphthalic anhydride, respectively[155].

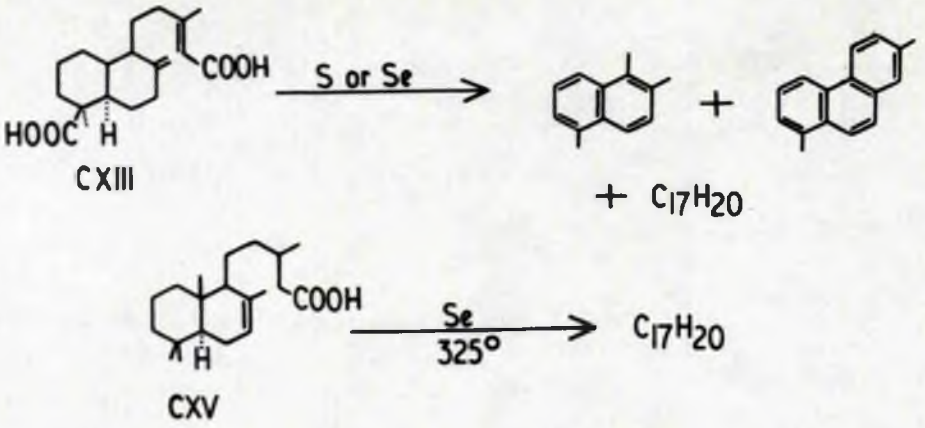
(ii) 3-, 6- and 9- Hydroxyperinaphthenone which, because of their symmetry, can give rise to only one methyl ether. 9-Hydroxy-perinaphthenone (LII)[85],[117] resists methylation owing to the effects of intra-molecular hydrogen bonding, but 3- and 6-methoxy-perinaphthenone (CVIII) and (CIX) have been characterised[154],[155]. In further substituted hydroxyperinaphthenones, in which the symmetry is destroyed, the tautomeric potentialities become apparent. Thus, 4-phenyl-6-hydroxyperinaphthenone (CX) affords two methyl ethers (CXI) and (CXII)[155].

(iii) 2-, 5- and 8-Hydroxyperinaphthenone, which do not show tautomerism. The 5- and 8- substituted compounds are unknown but

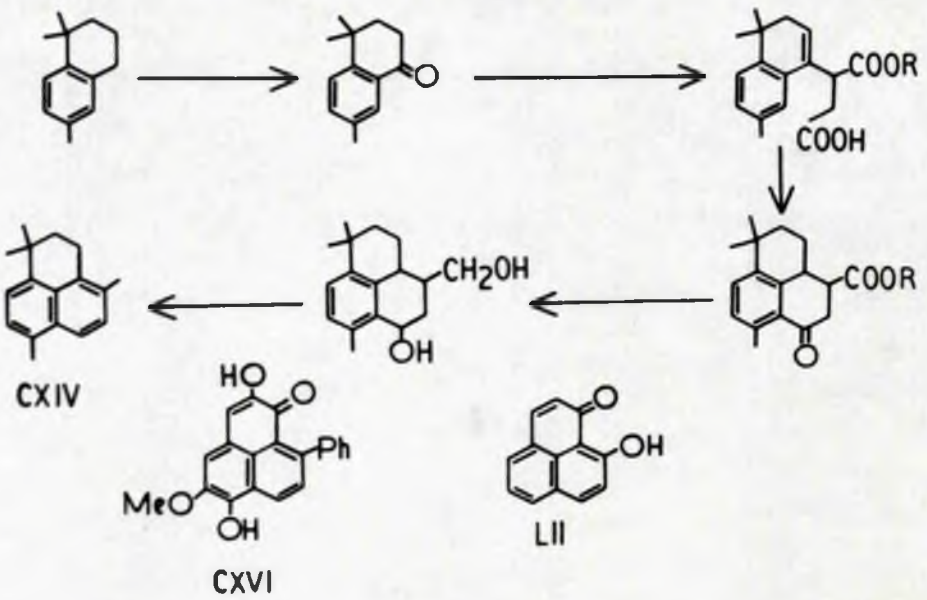
2-hydroxyperinaphthenone (LXIV)[81],[90] yields only one acetate and one benzoate[81].

The isomerisation of the perinaphthene molecule was elegantly demonstrated in 1957 by Nakazaki[136] who synthesised perinaphthene-2-C^{14} of specific activity 1.42$\mu c/\mu m$. On oxidation with potassium permanganate in acetone, naphthalic anhydride of specific activity 0.96$\mu c/\mu m$ was obtained. In order to eliminate the possibility that the loss in radioactivity was due to the formation of the symmetrical perinaphthenide anion during permanganate oxidation, a sample of the radioactive perinaphthene was oxidised to perinaphthenone using sodium dichromate in glacial acetic acid, and then further oxidised with potassium permanganate in acetone to naphthalic anhydride. The activity of this product was 0.92$\mu c/\mu m$. The loss of one-third of the radioactivity of perinaphthene on oxidation proves the ready tautomerisation of the molecule to make equivalent positions 2, 5 and 8.

The main conclusion to be reached from work on the isomerisation of perinaphthenes is that the perinaphthene nucleus behaves as a structural unit, making it exceedingly difficult to determine, in the case of the substituted perinaphthenes, which ring should properly be designated as the peri ring. Quite evidently, in the case of the simple perinaphthenes, the "extra" hydrogen tautomerises so readily that only the most stable of the various possible tautomers is isolated.



Synthesis of the hydrocarbon $C_{17}H_{20}$ (137):—



The Perinaphthene System in Nature.

A. II. 9. The Occurrence of the Perinaphthene System in Nature.

Until recently, perinaphthene and its derivatives held no interest for the natural products chemist. However, in 1954, Büchi and Pappas[137] showed by synthesis that the $C_{17}H_{20}$ hydrocarbon, which had been obtained along with the hydrocarbons agathalene (1,3,5-trimethylnaphthalene) and pimanthrene (1,7-dimethylphenanthrene) from the dehydrogenation of the terpenic acid, agathic acid (CXIII)[138], was 1,1,4,7-tetramethylperinaphthene (CXIV). This hydrocarbon was also obtained from another terpene, cativic acid (CXV), after dehydrogenation[139].

The 1,1,4,7-tetramethylperinaphthene thus obtained represents, however, a dehydrogenation fragment from a natural product. The actual occurrence of the perinaphthene system in nature was first reported by Cocks and Segal[140] in 1955. The naturally occurring glycoside, haemocorin, from the bulbous roots of Haemodorum corymbosum Vahl, afforded an unusual type of aglycone which, on the basis of chemical properties, degradative studies and a study of spectroscopic properties (ultra-violet and, significantly, infra-red), was found to be 2,6-dihydroxy-5-methoxy-9-phenyl-perinaphthenone (CXVI)[140],[135],[136].

It is considered that the fungal pigments, herqueinone[141], norherqueinone[141] and atrovenetin[141],[142] are derivatives of 9-hydroxyperinaphthenone (LII); the perinaphthene skeleton is also considered to be present in the wood pigments, pristimerin and celastrol[143].

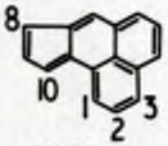
A, III, The cyclopenta [a] perinaphthene Structure.

As has been shown above (A,I), aromatic character is associated with the presence of stable π-electron systems which either exist in the ground state, as in the benzenoid hydrocarbons, or are capable of development during reaction, as in the azulenes. One π-electron system, the sextet, has served as an explanation for the aromatic stability of all of these hydrocarbons.

The fact that azulene was the only known aromatic hydrocarbon of its type meant that the seven-membered ring was the only known carbon framework which, by the delocalisation of a positive charge, made an effective contribution to the electronic stability of the molecule in the reacting state. There is, at present, only one known carbocycle, the five-membered ring, in which electronic stability is effected by delocalisation of a negative charge. Accordingly, a search was made for other aromatic hydrocarbons in which delocalisation of a stable π-electron system would occur over a positively or a negatively charged structure other than a simple seven- or five-membered ring. In particular, the perinaphthene nucleus appeared to be a satisfactory replacement for either of the rings as judged from a study of the compounds containing this nucleus.

The outstanding feature of perinaphthene chemistry is the tendency of the three six-membered rings to function as a structural unit in which a system of fourteen, thirteen or twelve π-electrons is delocalised over the skeleton during reaction. The modified carbonyl

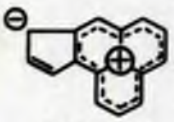
CXVII



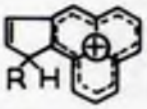
CXVIII

CXIX

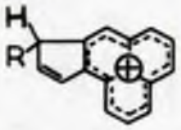
CXX



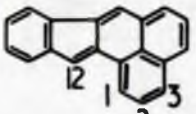
CXXI



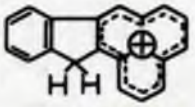
CXXII



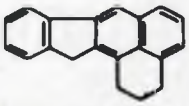
CXXIII



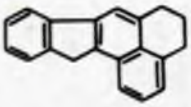
CXXIV



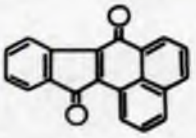
CXXV



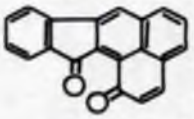
CXXVI



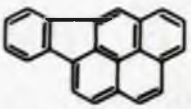
CXXVII



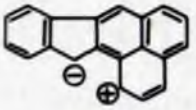
CXXVIII



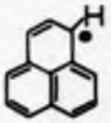
CXXIX



CXXX



CXXXI



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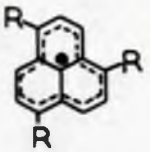
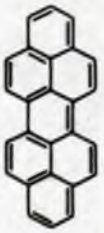
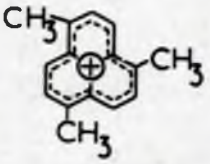


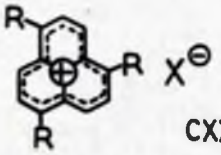
CXXXIII : R=H
CXXXIV : R=CH_3



LXVI



CXXXV



CXXXVI : R=H, X=I . CXXXVII : R=H, X=ClO_4
CXXXVIII : R=CH_3, X=ClO_4

properties of perinaphthenone, in particular the unusually high basicity and the abnormally low carbonyl stretching frequency (1637 cm^{-1}), indicate that the molecule is polarised to a great degree in the ground state and imply that considerable stability must be attributed to the perinaphthenylium cation (CXVII) in which twelve π-electrons are delocalised over the tricyclic framework of thirteen carbon nuclei. This view was substantiated by the isolation of the perinaphthenylium cation in the form of its salts (Reference 144 and Section C, VII).

The recognition of the stability of the cation (CXVII) led to the formulation[145],[146] of a new hydrocarbon, cyclopenta[a]-perinaphthene (CXVIII), which can be expected to show aromatic character of the azulene type. This hydrocarbon results from the fusion of the perinaphthene nucleus to a five-membered ring. In the limiting structure (CXIX), which reflects the direction of π-electron migration, twelve π-electrons are delocalised over the perinaphthene skeleton which takes the form of the perinaphthenylium cation, while a π-electron sextet is developed in the five-membered ring.

The 8- and 10- positions of cyclopenta[a]perinaphthene are not equivalent, in contrast to positions 1 and 3 in azulene. However, owing to the stability associated with the perinaphthenylium cation and the tendency of the cyclopentadiene ring to assume a negative charge, it is expected that structures (CXX) and (CXXI) will contribute to the ground state description of the molecule. One can therefore

predict that electron density will be highest at one or both of these positions and that electrophilic attack generally will take place at the same position (s), transition state stability arising from the formation, in the perinaphthene moiety, of the π-electron system of the perinaphthenylium cation, with which considerable stability is associated. The transition state is symbolised as formula (CXXII) or (CXXIII).

With a view to testing these predictions experimentally, indeno [2,1-a] -perinaphthene (CXXIV), a benzhomologue of (CXVIII), was synthesised and its properties studied[147],[129]. The most characteristic property of the hydrocarbon is its high basicity. It dissolves reversibly in strong acids e.g. in 72% perchloric acid and in 66% sulphuric acid, to form a green cation. A measure of the basicity, obtained by the procedure of Plattner et al.[148], placed indeno [2,1-a] -perinaphthene alongside the azulenes in order of basicity[149]. In the light of the reasoning outlined above, the conjugate acid is considered to possess structure (CXXV), proton addition at C_{12} being accompanied by the formation, in the perinaphthene nucleus, of the π-electron system of the perinaphthenylium cation (CXVII).

Electrophilic substitution occurs readily under conditions comparable in their mildness to those under which azulene undergoes similar substitution. Thus, indeno [2,1-a] - perinaphthene, on reaction with tetranitromethane at room temperature, forms a violet

mononitro compound; with acetyl bromide, it forms a monoacetyl derivative; and it couples with p-nitrobenzenediazonium chloride. The position of substitution has not been determined experimentally but it is considered, for reasons outlined above, to be position 12.

The hydrocarbon is readily reduced by zinc and acetic acid to a dihydro derivative, the structure of which is uncertain, or catalytically to a tetrahydro derivative which has been shown[129] to possess structure (CXXVI) or (CXXVII). The dihydroindeno [2,1-a] -perinaphthene undergoes with striking readiness a number of aromatisation reactions which reflects the aromatic character of indeno [2,1-a] -perinaphthene. When a solution of the dihydro derivative in benzene containing pyridine is treated at room temperature with osmium tetroxide, indeno [2,1-a] -perinaphthene is obtained in fair yield. The parent hydrocarbon is also reformed when a solution of the dihydro derivative in acetic acid is allowed to stand at room temperature in the presence of 20% palladised charcoal; in boiling solution, dehydrogenation is completed in a few minutes. Dehydrogenation also takes place readily when the dihydro derivative is boiled with an equimolecular amount of triphenylmethyl perchlorate in glacial acetic acid (C,XIII,5). When indeno [2,1-a] -perinaphthene is oxidised with chromic anhydride in acetic acid, it yields a quinone which has been shown, by a study of its spectral properties, to possess structure (CXXVIII) or (CXXIX)[129].

It was proved that positions 1 and 12 are involved in the ready

reaction of the hydrocarbon with dienophiles; thus, with maleic anhydride, it yields an adduct, ultimately transformed by dehydrogenation and decarboxylation into indeno [1,2,3-cd]-pyrene (CXXX). Other dienophiles which form adducts with indeno [2,1-a]-perinaphthene include 1,4-benzoquinone, 1,4-naphthoquinone, 7-bromobenzonaphthylene and benzyne (from o-bromo-fluorobenzene and magnesium in tetrahydrofuran). The very ready reaction of indeno [2,1-a]- perinaphthene with dienophiles indicates the ease with which a pair of π-electrons may be localised at C_1 and C_{12}. In accord with Robinson's views[150] on the mechanism of the Diels-Alder reaction, structure (CXXXI) must contribute significantly to the electronic description of the transition state.

In its chemical behaviour, indeno[2,1-a]-perinaphthene may be regarded as occupying a position between the benzenoid hydrocarbons and the azulenes.

A. IV. Present Work.

When the synthesis of indeno [2,1-a] -perinaphthene (CXXIV) had been successfully accomplished and the properties of the molecule studied[147],[139], a number of synthetic routes to the parent compound (CXVIII) were devised and investigated. However, all approaches to the cyclopenta [a] perinaphthene structure were frustrated, either by lack of reaction at a critical stage in the projected synthesis or by the unique properties and facile isomerisation of the perinaphthene nucleus and the ready formation of the perinaphthyl radical (CXXXII), in which thirteen π-electrons are delocalised over thirteen carbon atoms (CXXXIII).

This radical has been synthesised by a number of methods and its properties studied. Experimentally, it is observed that perinaphthyl is long lived and is relatively stable in solution as a blue entity which undergoes ready transformation in boiling benzene to peropyrene (LXVI). In order to shed some light on the mechanism of this transformation, 1,4,7-trimethylperinaphthyl (CXXXIV) was prepared by a ten-stage synthesis from 1,6-dimethylnaphthalene and its properties studied. In this derivative, such a transformation is impossible owing to the "blocking" effect of the three methyl groups.

A number of compounds containing the perinaphthenylium cation (CXVII), in which twelve π-electrons are delocalised over thirteen carbon nuclei, and the trimethylperinaphthenylium cation (CXXXV), have also been synthesised and their properties studied, in particular

the iodide (CXXXVI) and the perchlorates (CXXXVII) and (CXXXVIII).

A new method of dehydrogenation, limited in application by its specificity, has been studied, viz. dehydrogenation by removal of hydride ion followed by proton elimination, using triphenylmethyl perchlorate in glacial acetic acid.

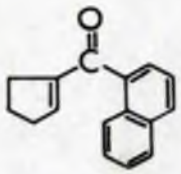
BI. Approaches to the cyclopenta [a] perinaphthene structure.

For reasons expounded in detail in (A, III), considerable interest attaches to the synthesis of cyclopenta [a] perinaphthene (CXVIII). The only known compound containing this ring system was indeno [2,1-a] perinaphthene (CXXIV) and this fact prompted attempts to synthesise cyclopenta [a] perinaphthene. Three synthetic routes to the molecule were devised and investigated but each approach was frustrated, due either to lack of reaction at a critical stage in the projected synthesis or to the unique properties and facile isomerisation of the perinaphthene nucleus.

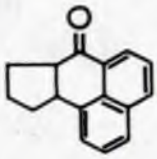
B.I.1. The Reaction of Naphthalene with cyclopentene-1-carboxylic acid chloride.

The approach to the cyclopenta [a] perinaphthene structure which proved to be the most promising utilised the Friedel-Crafts reaction between naphthalene and cyclopentene-1-carboxylic acid chloride.

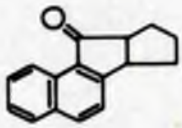
Variation in the site of substitution with experimental conditions is a striking feature of the chemistry of naphthalene. The oldest and most familiar instance, that of sulphonation, is complicated by the reversibility of the reaction, but this difficulty does not apply



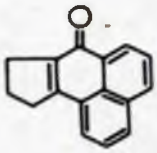
CXXXIX



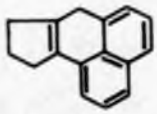
CXL



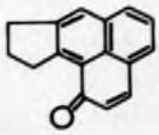
CXLI



CXLII



CXLIII



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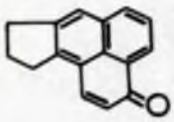
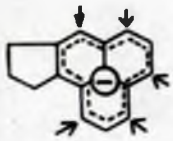
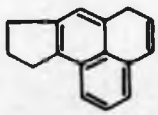


CXLV



CXLVI



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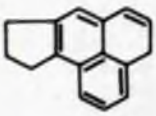
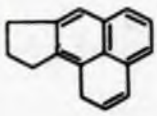
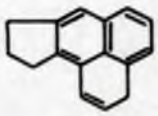


CXLVIII



CXLIX



CL

to the process of acylation in the presence of aluminium chloride in which similar variations have been observed. The literature on the acetylation and benzoylation of naphthalene by the Friedel-Crafts method has been summarised by Lock[151] and by Thomas[152] and is somewhat conflicting. Unfortunately, most of the reaction mixtures were heterogeneous and the relative extents of α and β substitution were seldom determined accurately.

Usually, aluminium chloride was added gradually to a mixture of acid chloride and hydrocarbon in carbon disulphide. Perrier[153], also employing carbon disulphide as a solvent, introduced the modification of first forming the acid chloride - aluminium chloride complex and subsequently adding the hydrocarbon. This procedure involves warming a mixture of the two chlorides, alone or in the presence of carbon disulphide, and although satisfactory with some acid chlorides e.g. benzoyl chloride[154], is unsatisfactory for general application owing to the low solubility of the complexes in carbon disulphide.

This difficulty was, however, overcome by Baddeley[155] who used solvents in which homogeneous solutions are readily obtained at ordinary temperatures. It was found that, in ethylene and methylene chlorides, almost pure α-naphthyl ketones were obtained in the absence of reagents which combined with the aluminium chloride - acid chloride complex.

In attempts to obtain α-naphthoylcyclopent-1-ene (CXXXIX) by the Friedel-Crafts reaction between cyclopentene-1-carboxylic acid

chloride and naphthalene, either methylene chloride or 1,2-dichloroethane was used as solvent, for reasons outlined above. No difficulty was experienced in obtaining a product in 30% yield by adding the hydrocarbon to a solution of the acid chloride - aluminium chloride complex and carrying out the reaction either at room temperature or at the boiling point of methylene chloride. The nature of the product of this reaction was investigated by oxidative degradation using both potassium permanganate in acetone and sodium dichromate in glacial acetic acid; the degradation product was an acid mixture as evidenced by the wide (30°) melting range. This indicated that the ketonic product from the Friedel-Crafts reaction was a mixture of at least two of α-naphthoylcyclopent-1-ene (CXXXIX), 2:3-cyclopentanoperinaphthen-1-one (CXL) and the compound (CXLI), the latter products being formed by peri and β cyclisation of (CXXXIX) under the influence of aluminium chloride. Exclusive α-substitution in the naphthalene nucleus is assumed, in the light of the results obtained by Baddeley[153].

The view that the product of the Friedel-Crafts reaction was a mixture of ketones was substantiated by a study of the infra-red spectrum which showed carbonyl absorption bands at 1647 cm^{-1} (αβ - unsaturated carbonyl) and at 1701 cm^{-1} (six-membered ring carbonyl). There was no evidence in the infra-red for the carbonyl absorption frequency of a five membered ring ketone which usually falls in the region 1750 - 1745 cm^{-1} [156].

The ketonic product afforded, in low yield, a 2:4-dinitrophenylhydrazone, which was homogeneous.

Baddeley's work[155] seemed to indicate that the gradual addition of aluminium chloride to a mixture of the acid chloride and naphthalene must result in considerable β substitution especially during the first part of the reaction. A number of control reactions were carried out under conditions more forcing than those described above, viz. at the boiling point of 1,2-dichloroethane and in the presence of three molecular proportions of aluminium chloride, with the intention of ring closing and/or dehydrogenating the primary product of the reaction to 2:3-cyclopentenoperinaphthenone (CXLII). In one case only, when aluminium chloride was added to a solution of the acid chloride and naphthalene, was this successfully accomplished, albeit in low yield. The desired product, accompanied by a mixture of other ketones, was easily isolated by virtue of its solubility in concentrated hydrochloric acid; it showed the low carbonyl absorption frequency in the infrared (1634 cm^{-1}), characteristic of perinaphthenones (Table I). Other control reactions, in which the Perrier complex was preformed, produced intractable tars from which no useful products could be isolated.

However, this successful run could not be repeated. The fact that a mixture of (CXXXIX) and (CXL) was isolated in 50% yield when cyclopentene-1-carboxylic acid chloride was allowed to react with naphthalene in the presence of three molecular proportions of

aluminium chloride at room temperature, indicated that the primary reaction, formation of α-naphthoylcyclopent-1-ene, was taking place. No reasonable explanation can be offered for the inability to repeat the experiment which yielded 2:3-cyclopentenoperinaphthenone. The view that excess aluminium chloride at 80° may have caused destruction of the double bond in (CXXXIX) was rejected in the light of the results of Baker and Jones[157] who successfully cyclised 1-benzoylcyclopentene with three molecular proportions of aluminium chloride at 80°.

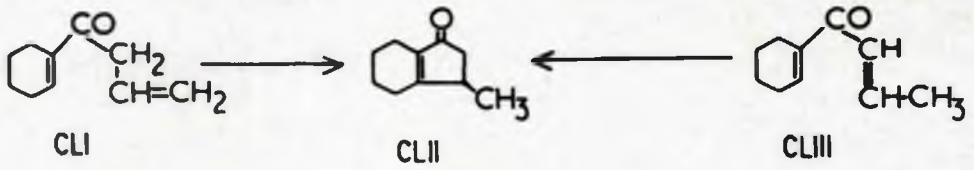
A number of attempts were then made to cyclise and/or dehydrogenate the mixture of (CXXXIX) and (CXL) to 2:3-cyclopentenoperinaphthenone. However, each of the attempts was fruitless, no more than a negligible amount of the desired product being obtained.

Elimination of oxygen from 2:3-cyclopentenoperinaphthenone (CXLII) by the use of lithium aluminium hydride[105],[158] afforded a cyclopentenoperinaphthene to which structure (CXLIII) is arbitrarily assigned. The melting point of the product indicates that it is a mixture of isomeric hydrocarbons. Similar reduction of the cyclopentenoperinaphthenone (CXLIV) or (CXLV)[120] yielded a product which likewise melted over a large range. (CXLIII) did not depress the melting point of this product. It therefore seems likely that in each case a mixture of isomeric cyclopentenoperinaphthenes was produced. This belief was strengthened when the hydrocarbon products obtained by the lithium aluminium hydride reduction of (CXLII) and (CXLIV) or (CXLV) were in turn re-oxidised using sodium dichromate in glacial

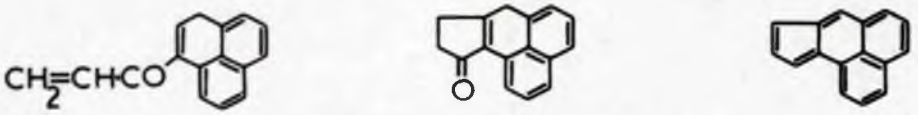
acetic acid[139]. The cyclopentenoperinaphthanones obtained were, in each case, mixtures of isomeric ketones as indicated by their melting points.

The production of an isomeric mixture of hydrocarbons is not surprising in view of the mechanism of the hydride reduction. The intermediate anion (CXLVI) is stabilised by delocalisation of the negative charge over the perinaphthene moiety; the possible positions for proton addition arise because of the electron releasing character of the trimethylene ring and are indicated by arrows in (CXLVI). Any one of the five reaction products (CXLIII), (CXLVII), (CXLVIII), (CXLIX) and (CL) is thus possible. However, preferential formation of one of these products was expected in view of the results obtained by Bockelheide and Larrabee[131] on the isomerisation of the methyl perinaphthenes. In this case, it was expected that the thermodynamically most stable isomer (CXLIII), containing a highly substituted peri double bond in the perinaphthene moiety, would be formed exclusively.

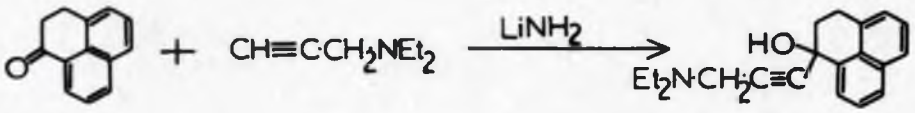
Thus, while the hydrocarbons obtained by the reduction of (CXLII) and (CXLIV) or (CXLV) have been named 2:3-cyclopentenoperinaphthene and 8:9-cyclopentenoperinaphthene, respectively, it should be borne in mind that they are isomeric mixtures. These examples provide another instance of the ready isomerisation of the perinaphthene nucleus (A,II,B) arising, in this case, as a result of the stability and symmetry of the perinaphthenide anion.



CLI CLII CLIII

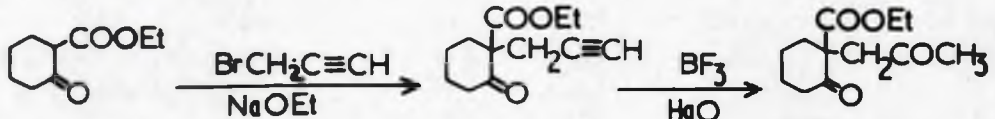


CLIV CLV CXVIII

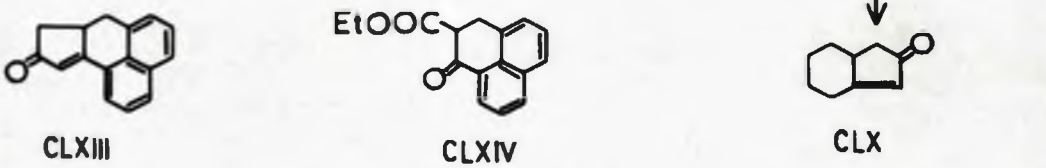


L CLVI CLVII

CLVIII CLIX



CLXII CLXI



CLXIII CLXIV CLX

Attempts to dehydrogenate 8:9-cyclopentenoperinaphthene to cyclopenta [a] perinaphthene (CXVIII), catalytically, under a variety of conditions or chemically by heating with sulphur, gave no useful product[129]. When bromination with N-bromosuccinimide was carried out as the initial step in an attempted bromination - dehydrobromination procedure, formation of the transient cyclopentenoperinaphthyl radical was observed.

B. I. 2. The Projected Synthesis of 10-Oxo-7,8,9,10-Tetrahydro-cyclopenta [a] perinaphthene.

A versatile route to hydroaromatic structures containing five-membered rings, which has been developed by Nazarov, consists in the cyclisation of substituted allyl vinyl and divinyl ketones to substituted cyclopentanones, the most widely used procedure involving treatment with a hot mixture of phosphoric and formic acids. For instance, allyl cyclohexenyl ketone (CLI) is converted into 4,5,6,7-tetrahydro-3-methyl-indanone (CLII) and the corresponding divinyl ketone (CLIII) gives the same product. The mechanism of the reaction has been discussed by Braude and Coles[160] who concluded that the prime function of the acid medium is that of a proton donor and that the

ethylenic compound, acting as a weak base, is partly converted into a carbonium ion by the reversible addition of one or more protons; this mechanism is in accord with the fact that ketones (CLX) and (CLXIII) yield the same product on cyclisation.

The wide applicability of this reaction suggested its use in the cyclisation of the divinyl ketone (CLXV) to 10-oxo-7,8,9,10-tetrahydrocyclopenta[a]perinaphthene (CLXV). The perinaphthene skeleton in this molecule would not be expected to undergo ready isomerisation owing to the stabilising effect of the carbonyl group in conjugation with the peri double bond; little difficulty is anticipated in converting this compound, once obtained, into its reduction and dehydrogenation product, cyclopenta[a]perinaphthene (CXVIII). A route to the divinyl ketone (CLXV) was suggested by the synthesis by Islam and Raphael of compounds containing the bicyclo[5:3:0]-decane system from cycloheptanone[161].

Condensation in liquid ammonia of perinaphthen-1-one (L) and the lithium salt of 3-diethylaminoprop-1-yne (CLVI), prepared *in situ* by treatment of 2-bromo-3-diethylaminoprop-1-ene with two moles of lithamide, gave 1-(3-diethylaminoprop-1-ynyl)-perinaphthen-1-ol (CLVII) in good yield. Thereafter, it was expected that the acetylenic alcohol (CLVII) could be induced to undergo dehydration to (CLVIII), followed by hydration of the triple bond yielding (CLIX). Ready elimination of the diethylamine group β to the carbonyl group in (CLIX) would lead to the production of the desired divinyl ketone

(CLIV). However, all attempts to obtain the substituted perinaphthene (CLVIII) by dehydration of 1-(3-diethylaminoprop-1-ynyl)-perinaphthan-1-ol (CLVII) were to no avail, although a product of unknown constitution was obtained when dehydration was attempted using a mixture of formic and phosphoric acids.

Conversion of the alcohol (CLVII) to the ketone (CLV) in one step, a process which had been achieved with the corresponding intermediates in the bicyclo [5:3:0] decane system[161] was attempted unsuccessfully.

B, I, 5. The Projected Synthesis of 9-Oxo-7,7a,8,9-Tetrahydro-cyclopenta [a] perinaphthene.

Islam and Raphael[162] have described a method for the synthesis of bicyclo [4:3:0] non-6-en-8-one (CLX) by hydrolysis, decarboxylation and ring closure of the diketo ester (CLXI) using dilute alkali. The diketo ester (CLXI) was prepared by hydration of the triple bond in the product of the reaction of ethyl 2-carboxycyclohexanone (CLXII) with propargyl bromide in the presence of sodium ethoxide.

An attempt was made to build the skeleton of the cyclopenta[a]-perinaphthene molecule, in the form of the $\alpha\beta$ unsaturated ketone, 9-oxo-7,7a,8,9-tetrahydrocyclopenta [a] perinaphthene (CLXIII) by the

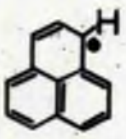
application of a similar series of reactions to ethyl 2-carboxy-perinaphthan-1-one (CLXIV).

Ethyl hydrogen α-naphthylmethyl malonate was prepared by hydrolysis of diethyl α-naphthylmethyl malonate using sufficient alkali to hydrolyse only one of the ester groups. The product was the half ester as indicated (i) by the working up process (C,III,1) and (ii) by a determination of saponification and neutralisation equivalents.

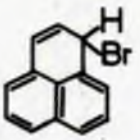
This was cyclised to ethyl 2-carboxyperinaphthan-1-one (CLXIV) by the use of anhydrous liquid hydrogen fluoride. The reaction times and temperatures were varied systematically in order to find the best reaction conditions. However, the percentage conversion to the keto ester was always small and the conditions described (C,III,2) are those which gave the maximum yield obtained. This was not a major obstacle as the unreacted half ester was always recovered. A satisfactory analysis could not be obtained for the product of cyclisation, purified by vacuum distillation in a closed system. The percentages determined by experiment for carbon and hydrogen were invariably higher than required, a fact which seemed to indicate that some decarboxylation took place during purification. There was no evidence for dehydrogenation to the corresponding ethyl carboxy-periraphthenone.

Attempts to condense this product with propargyl bromide always yielded a yellow oil which appeared to be identical with the starting

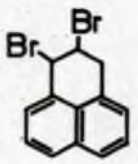
material. Thus, it yielded a similar colouration with ferric chloride solution and the analytical figures were almost identical with those obtained for ethyl 2-carbomycarinaphthum-1-one.



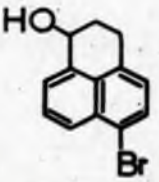
CXXXII



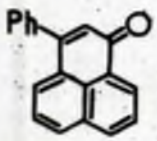
CLXV



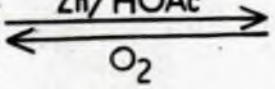
CLXVI

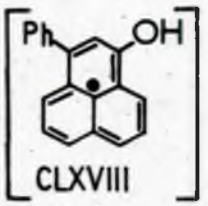


CLXVII

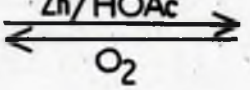


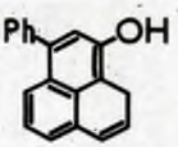
CLXIX



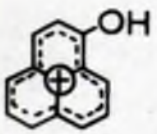


CLXVIII

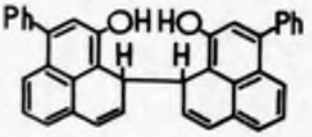




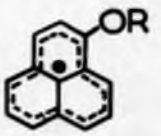
CLXXI



LXXXII



CLXX



CLXXII : R=$COCH_3$

CLXXIII : R=COC_6H_5

CLXXIV : R=CH_3

B II. The Radical and Ions derived from Perinaphthene.

B II. 1. Introduction.

The two most important factors responsible for the stabilisation of long lived free radicals are considered to be the added resonance stabilisation of the radical over that of its dimer and the steric effect which leads to bond lengthening and weakening in the dimeric form. In the perinaphthyl radical (CXXXII), the high degree of symmetry makes possible a considerable amount of resonance stabilisation although there should be little or no steric hindrance to its dimerisation.

With a view to studying these factors independently of each other, Doskeland and his co-workers[105],[163] made a number of unsuccessful attempts to prepare perinaphthyl. Attempts to prepare 1-bromoperinaphthene (CLXV) as a key intermediate in the preparation of the radical, were unsuccessful. Bromination of perinaphthene in the cold readily gave 2,3-dibromoperinaphthene (CLXVI) but attempts to dehydrobrominate the dibromo compound yielded deeply coloured green-blue solutions from which no monobromo compound could be isolated[105]. All attempts to convert 3-bromoperinaphthen-1-ol (CLXVII) to a bromoperinaphthene were also unsuccessful, highly coloured amorphous solids being formed[163].

Four oxygenated derivatives of perinaphthyl have previously been

reported. Koelsch and Anthes[117] postulated the existence of the red 1-hydroxy-3-phenylperinaphthyl (CLXVIII) as an intermediate in the reduction of 3-phenylperinaphthenone (CLXIX). The reduction of (CLXIX) with zinc and acetic acid proceeded in two separate stages, in each of which one atom of hydrogen was taken up. The first product, 1,1'-bi-(7-phenyl-9-hydroxyperinaphthyl) (CLXX) was isolated as crystalline red solid melting at 127-128° which showed a molecular weight in melted camphor corresponding to a monomeric radical or a semiquinone; this low molecular weight was considered to be due to disproportionation into 3-phenylperinaphthenone and 7-phenyl-9-hydroxyperinaphthene (CLXXI). The second product of the reduction of 3-phenylperinaphthenone was (CLXXI), a colourless solid melting at 136-138°, which reacted readily with oxygen to give (CLXX) and later (CLXIX). 3-Phenylperinaphthenone (CLXIX) reacted with an equivalent amount of (CLXXI) in ligroin to give (CLXX) quantitatively. The structures assigned to these compounds are supported by the reduction potentials.

Three simple derivatives of perinaphthyl have been reported by Clar[164]. Treatment of an ethereal solution of perinaphthenone with acetyl or benzoyl chloride followed by reduction with zinc or, better, with activated magnesium, resulted in the production of a deep blue colouration presumed to be due to the presence of 1-acetyloxy or 1-benzoyloxy-perinaphthyl (CLXXII) and (CLXXIII), respectively. On chromatography of a solution of perinaphthenone in methanol which has been treated with anhydrous hydrogen chloride, the eluates have been

observed to possess a deep blue colouration believed to be due to 1-methoxyperinaphthyl (CLXXXIV). Attempts to isolate solid products from the above resulted in the formation of polymeric material.

After the publication of a preliminary communication from this laboratory[166] describing part of the work embodied in this thesis, the existence of perinaphthyl was claimed in a solution of perinaphthene in carbon tetrachloride which had been sealed in air and stored for several months. The electron spin resonance spectrum of perinaphthyl was reported on the basis of determinations made with this solution[166]. However, the properties of the radical as reported below shed considerable doubt on its existence under the conditions specified.

Polarographic investigation of the first wave of perinaphthenone and a number of simple derivatives has shown that reduction proceeds reversibly and with remarkable ease compared with the corresponding process in benzanthrone and benzalacetophenone[125]. The essential process is a one-electron addition to the molecule with formation of 1-hydroxyperinaphthyl. Perinaphthenone-3-carboxylic acid displays greater ease of radical formation than does the parent ketone and it is presumed that the electron attracting effect of the carboxyl group promotes electron addition at the oxygen site, thus shifting the half step potential to less negative values, an effect which disappears when the carboxylate ion is formed. On the other hand, 9-hydroxy-perinaphthenone shows considerable resistance to radical formation compared with the parent ketone and it is suggested that strong

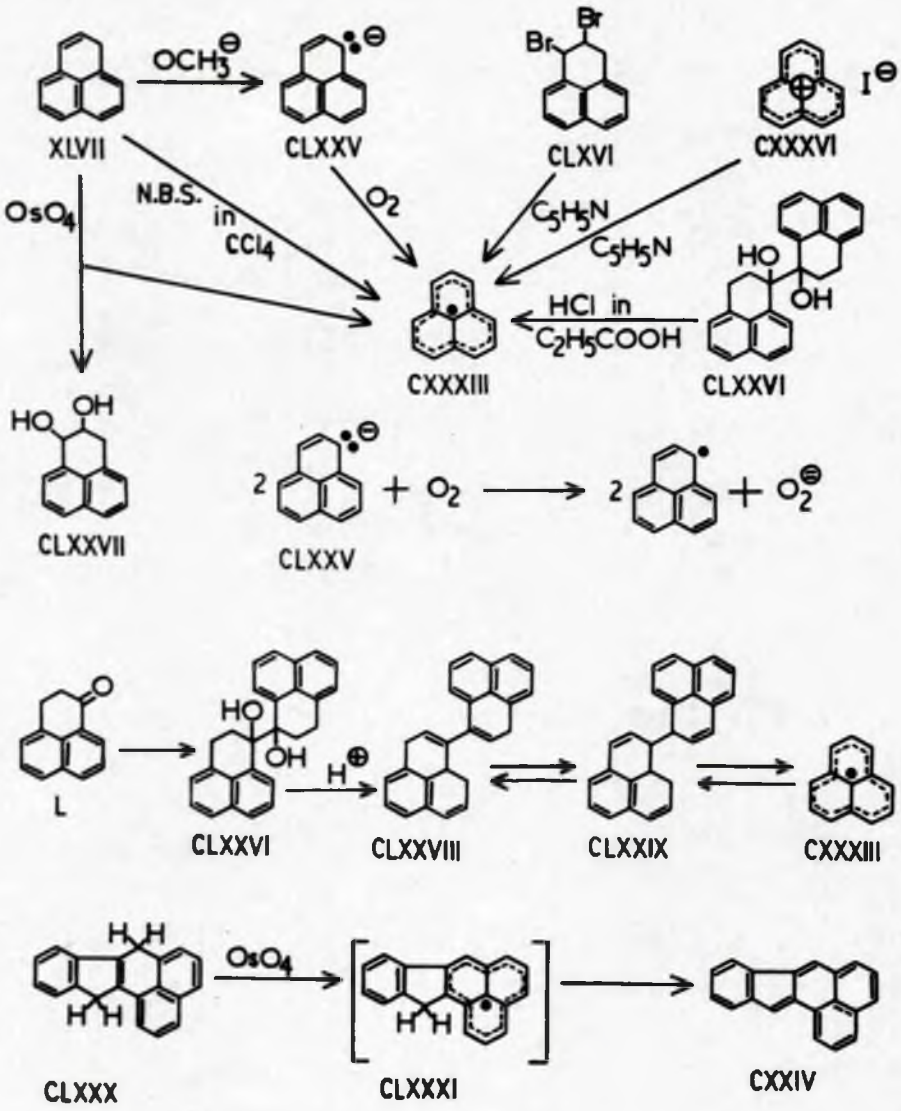
hydrogen bonding supplies additional resonance energy to the hydroxy compound.

The pKa value of the conjugate acid (LXXXII) of perinaphthenone was determined spectroscopically by partitioning the ketone between mixtures of chloroform and sulphuric acid corresponding to various Hammett function values (Ho). The results are indicative of the ready formation of the hydroxyperinaphthenylium cation as compared with the cations derived from benzanthrone and benzalacetophenone. The data from these investigations are tabulated below.

The Half-Wave Potentials and Acidity Constants of Perinaphthenone and its Derivatives(125)

	$-E_{\frac{1}{2}}$ V(S.C.E.)	pKa (conjugate acid)	pKa (free radical enol).
perinaphthenone	0.54	-3.9	9.5
perinaphthenone-3-carboxylic acid	0.24	-3.4	-
perinaphthenone-3-carboxylate (ion)	0.54	-	9.0
9-hydroxyperinaphthenone	0.62	-4.8	8.0
perinaphthenone-9-oxide (ion)	0.49	-	13.0
benzanthrone	0.47	-5.8	10.6
benzalacetophenone	0.52	-7.6	10.4

Preparations of Perinaphthyl.



B, II, 2. The Preparation of Perinaphthyl.

The formation of the perinaphthyl radical (CXXXXIII) has been observed in six distinct reactions, as follows:-

(i) In the best method for the preparation of perinaphthyl, the red perinaphthenide anion (CLXXV) was shaken at room temperature in the presence of oxygen.

(ii) The addition of a catalytic amount of concentrated hydrochloric acid to a solution of the diol (CLXXVI) in propionic acid at room temperature resulted in the immediate formation of the blue perinaphthyl.

(iii) Treatment of 1,8-dibromoperinaphthene (CLXVI) with organic bases resulted in the loss of hydrogen bromide and bromine and the formation of perinaphthyl.

(iv) Perinaphthyl was formed when perinaphthene was treated with N-bromosuccinimide.

(v) Perinaphthyl was formed along with the normal product, cis 1,8-dihydroxyperinaphthene (CLXVII) when perinaphthene was allowed to react with osmium tetroxide and pyridine in benzene solution.

(vi) Perinaphthenylium iodide (CXXXVI), when dissolved in pyridine, yielded perinaphthyl.

B, II, 2 (a). Oxygenation of the perinaphthenide anion (CLXXV):

The red perinaphthenide anion (CLXXV), prepared from perinaphthene and potassium methoxide in 2% ethereolic ether solution, was shaken at room temperature in the presence of oxygen. Perinaphthyl arose in the process by a spontaneous one-electron transfer from the anion (CLXXV) to molecular oxygen.

In preparations of perinaphthyl by this method, it was observed that perinaphthyl itself reacts with oxygen. A typical oxygenation curve, Plate I, shows that the radical takes up oxygen much more slowly than the anion. As can be seen from Plate II, the plot of oxygen absorbed against time is not linear up to the point indicating complete conversion from anion to radical; this slight deviation from linearity as the concentration of radical increases is considered to be due to the reaction of perinaphthyl with oxygen (C,V). However, the difference in the reaction rates between the anion (CLXXV) and the radical (CXXXIII) allows the primary reaction to be used in the preparation of perinaphthyl. Since the removal of unchanged perinaphthene is difficult, while the products derived from perinaphthyl e.g. peroxide (C,V) are readily removed, absorption of oxygen was allowed to take place in slight excess of the amount required for the theoretical completion of the primary step.

Quantitative formation of the peroxide ion, which is implied in the above reaction, was shown to take place. The concentration of peroxide ion which was formed by allowing varying amounts of oxygen

to be absorbed by a solution of the anion (CLXXV), was determined analytically by titration against standard sodium thiosulphate solution. Plate XXI shows a plot of the peroxide ion concentration, determined analytically, against peroxide ion concentration calculated from the volume of oxygen absorbed. The results obtained lie close to the theoretical straight line which represents quantitative peroxide formation.

B, II, 2 (b). Perinaphthyl from 1,1′-diperinaphthen-2-ol (CLXXVI):

This synthesis, of theoretical significance since it demonstrates the reversible dissociation of perinaphthyl, started from the diol (CLXXVI) which was obtained by a bimolecular reduction of perinaphthen-2-one using aluminium amalgam in a mixture of ethanol and benzene[167]. It is of interest that the hydroxyl band in the infra-red spectrum of (CLXXVI) is at an unusually high frequency for a solid (3570 cm^{-1}). This probably arises because the highly hindered nature of the hydroxyl groups makes intermolecular hydrogen bonding impossible.

The addition of a catalytic amount of concentrated hydrochloric acid to a solution of the diol (CLXXVI) in propionic acid at room temperature resulted in the immediate formation of perinaphthyl (CLXXXIII). Under the conditions of the reaction, the diol is dehydrated to 3,3′-diperinaphthyl (CLXXVIII). Acid-catalysed

prototropic rearrangement yields the isomer (CLXXIX), the dienoic form of perinaphthyl. This is followed by spontaneous fission of the carbon-carbon bond linking the perinaphthene moieties in (CLXXIX), yielding perinaphthyl.

The ready formation of perinaphthyl from 1,1'-diperinaphthen-1-ol by the mechanism outlined above is in conformity with the ease of reversible one-electron addition observed in the polarographic reduction of perinaphthenone[123].

B, XI, 2 (c). Perinaphthyl from 1,2-dibromoperinaphthene, and from perinaphthene by treatment with N-bromosuccinimide:

It has already been indicated that the red perinaphthenide anion (CLXXV) may be obtained as its lithium or potassium derivative. In this connection, it was observed that on application of the Vanzetti colour test[108] which involves formation of the anion, a blue green colour developed[105]. In addition, a similar colour resulted in the attempted dehydrobromination of 1,2-dibromo-perinaphthene (CLXVI) and on treatment of perinaphthene with N-bromo-succinimide[105]. It has now been shown that the entity responsible for colour development in the above cases is the perinaphthyl radical (CLXXXII). Such a colour was also observed when perinaphthene was treated with triphenylmethyl[105] and when 9-bromoperinaphthenol (CLXVII) was subjected to dehydration using ethanolic hydrogen

chloride[163]. Thus, although Boekelheide and his co-workers[105], [165] were not unsuccessful in their attempts to form perinaphthyl, they failed to realise the significance of the deep blue-green solutions they obtained.

B,II,2 (d). The action of osmium tetroxide on perinaphthene:

In the reaction of perinaphthene with osmium tetroxide, it was observed that two processes were taking place simultaneously. Thus, although most of the perinaphthene was consumed in the form of an adduct from which 1,2-dihydroxyperinaphthene (CLXXVII) was eventually isolated, this reaction was attended by the formation of perinaphthyl. Part of the perinaphthyl formed was converted during the chromatographic procedure to peropyrene (LXVI); the remainder was characterised as perinaphthenylium iodide (CXXXVI) (C,IV,8).

This rather unusual reaction shows a parallel with the reaction of osmium tetroxide with dihydroindeno [2,1-a]-perinaphthene (CLXXX)[129],[146]. In an attempt to locate and open the most localised double bond of dihydroindeno [2,1-a]-perinaphthene, the compound was reacted with osmium tetroxide. Unexpectedly, this attempt to hydroxylate (CLXXX) led to the formation of a significant amount of indeno [2,1-a]-perinaphthene (CXXIV), together with a product of unknown structure. The formula (CLXXX), given for

dihydroindeno [2,1-a]-perinaphthene is tentative for the structure of the compound has not yet been ascertained.

Osmium tetroxide is acting in these reactions in the somewhat unusual role of a dehydrogenating agent. Formation of perinaphthyl by this method is a reflection on the tendency of perinaphthene to undergo radical formation. This suggests that a substituted perinaphthyl radical (CLXXXI) exists as an intermediate in the dehydrogenation of dihydroindeno [2,1-a]-perinaphthene; the loss of a hydrogen atom from (CLXXXI) is energetically favoured and therefore spontaneous since the product is the aromatic indeno [2,1-a]-perinaphthene.

These instances of osmium tetroxide functioning as a dehydrogenating reagent by a radical mechanism find no parallel in the chemical literature.

B,II, 2 (e). Perinaphthyl from Perinaphthenylium Iodide:

This reaction is discussed in B,II,4.

B. II. 3. The Properties of Perinaphthyl.

B, II, 3 (a). General Properties:

Perinaphthyl is green in the solid state but has not in this form been isolated pure. It is extremely sensitive to heat and undergoes ready transformation in boiling ether or benzene to peropyrene (LXVI). It has therefore not been possible to recrystallise the crude preparations nor to determine the melting point of the radical.

Perinaphthyl is obtained in solution as a blue entity and is a relatively stable free radical. The ready formation of perinaphthyl in the reactions described above indicates the presence of a delocalised π-electron system, leading to a high degree of resonance stabilisation, in free radicals of the perinaphthene series. This conclusion is supported by the failure of perinaphthyl to react with nitric oxide.

The absorption spectrum of perinaphthyl in ether solution was examined in the region 750-500 mμ. The radical showed a broad absorption maximum at 610-615 mμ with a flat peak at 612-615 mμ. Plate IV shows the spectrum of perinaphthyl prepared from the perinaphtheride anion; the spectra of solutions of the radical prepared from perinaphtherylium iodide and from perinaphthene by the

action of N-bromosuccinimide were identical in the region 750-500mμ.

B,II, 5 (b). The Dimerisation and Disproportionation of Perinaphthyl:

The formation of perinaphthyl from the diol (CLXXVI) and the conversion of perinaphthyl to peropyrene (LXVI) together indicate that an equilibrium exists between perinaphthyl and its dimeric form. It has been found that the dimeric form disproportionates into peropyrene and a hitherto unidentified hydroaromatic product. This irreversible process takes place slowly at room temperature but is completed in a few seconds in boiling benzene or glacial acetic acid. The thermal instability of the dimeric form of perinaphthyl thus accounts for the earlier failures to prepare this radical.

A spectrophotometric study of the dimerisation and disproportionation of perinaphthyl was undertaken (C,IV,9). The optical density at 615 mμ of a solution in the radical in ether was measured at various time intervals after an arbitrary fixed time, the time when the radical solution first began to issue from the chromatographic column, when the concentration of the solution was assumed to be 100% with respect to the radical and 0% with respect to the dimeric form. The decrease in the optical density at 615 mμ with time is shown on Plate V.

The unpaired electron in the perinaphthyl radical may, in theory,

becomes localised on any one of the thirteen carbon atoms of the framework. These thirteen positions can be divided into four groups as follows:

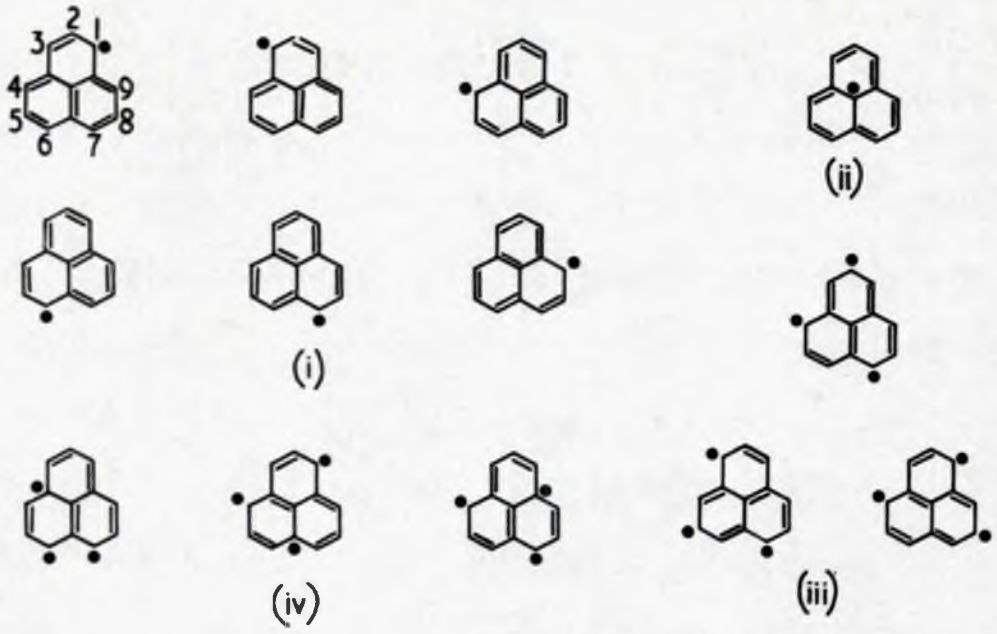
(i) The unpaired electron can be localised on one of the six equivalent carbon atoms 1,3,4,6,7 or 9. These positions are energetically favourable since the remainder of the carbon skeleton can assume a stable structure.

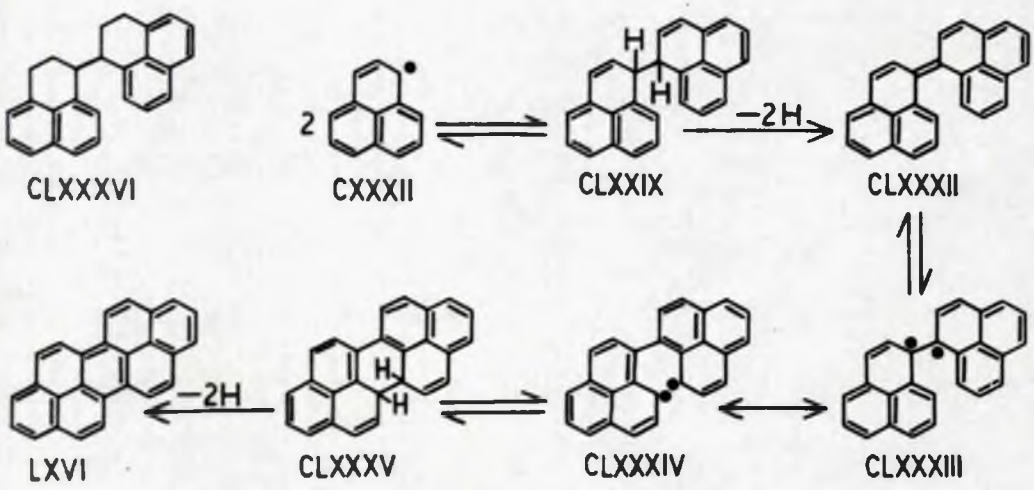
(ii) The unpaired electron can be localised on the central carbon atom. This structure is again energetically favourable for the same reason.

(iii) In this class, the "odd" electron is localised on one of the three equivalent positions 2,5 and 8. However, these positions are not energetically favoured for localisation since no structure can be assumed in which fewer than three carbon atoms carry unpaired electrons.

(iv) The class in which the "odd" electron is localised on one of the three angular carbon atoms is also energetically unfavourable since, once more, the carbon framework must carry at least two other unpaired electrons.

Hence, dimerisation of perinaphthyl may take place through the limiting structures in groups (i) and (ii) but not (iii) and (iv). However, structure (ii) does not permit the formation of a stable dimer for steric reasons. Thus, only structures of the type present in group (i) need be considered as positions for the localisation of


2
1
3
4
9
5
8
6
7
(ii)
(i)
(iv)
(iii)


CLXXXVI
2
CXXXII
H
H
CLXXIX
−2H
CLXXXII
−2H
LXVI
H
H
CLXXXV
CLXXXIV
CLXXXIII

the unpaired electron in the dimerisation of perinaphthyl.

Perinaphthyl (CLXXXXI) is in equilibrium with its dimeric form (CLXXXX) as represented opposite. The loss of four hydrogen atoms is incurred in the formation of peropyrene (LXVI) from perinaphthyl. The mechanism formulated opposite seems energetically reasonable. Creation of a double bond between the two perinaphthyl moieties by the loss of two hydrogen atoms from the dimeric form of perinaphthyl gives the diperinaphthenylidene structure (CLXXXII) which sets up an equilibrium with the diradical structure (CLXXXXI) by the uncoupling of two electrons from the double bond. This process is aided by the added resonance stabilisation due to the delocalisation of the two "odd" electrons over the two perinaphthyl moieties. A further equilibrium is set up between the diradical form (CLXXXIV) and the dihydroaromatic intermediate (CLXXXV) by a coupling of the two unpaired electrons. The last step in the sequence proceeds irreversibly with a gain in stability due to the aromatisation of the dihydroaromatic structure (CLXXXV) and formation of peropyrene (LXVI).

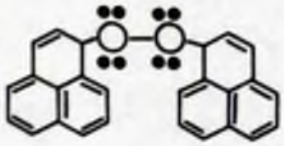
Peropyrene is very sparingly soluble in perpionic acid. Hence, the yield of peropyrene obtained by the dehydration of the diol (CLXXVI), averaging 24 mgs. per 100 mgs. of diol used (27%) is considered to be close to that of the total peropyrene formed. Further, a colourless or pale yellow product was isolated along with peropyrene by dehydration of the diol (CLXXVI) (C,IV,7). This was much more soluble than peropyrene in organic solvents such as benzene,

propionic acid and acetone; however, light petroleum tended to throw it out of solution as an amorphous solid or as an oil. The very small quantity obtained prevented the characterisation of this product but it seems likely that it is a polyhydroxyperinaphthen-1-yl with a structure similar to (CLXXXVI), formed along with peroxyxene by the irreversible disproportionation of the dimeric form of perinaphthyl.

B, II, 3 (c). The Oxygenation of Perinaphthyl:

As has been indicated above (B,II,2(a)), perinaphthyl reacts with oxygen although the radical takes up oxygen much more slowly than the perinaphthenide anion, as is shown by a typical oxygenation curve (Plate I).

The products formed by the oxygenation of perinaphthyl are perinaphthenone (XLVIII) and perinaphthyl peroxide, the molecular formula of which is $C_{20}H_{12}O_2$. In one reaction (C,V,1), oxygenation of the perinaphthenide anion was continued until sufficient oxygen had been absorbed for complete conversion of the resulting perinaphthyl to the dark green peroxide. The peroxide mass was well washed with ether and from the dark green ether washings an orange red solid was obtained; this yielded perinaphthenone after sublimation. It is probable that the deep green colour of the ether washings was conferred on the solution by some unchanged perinaphthyl in the presence of yellow perinaphthenone.



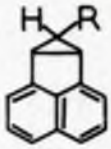
CLXXXVII

CXXXVI
violet-black

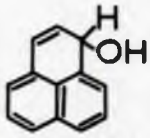
$I^{\ominus}$ $\xrightarrow[CH_3NO_2]{AlX_3\ in}$ 

green solutions

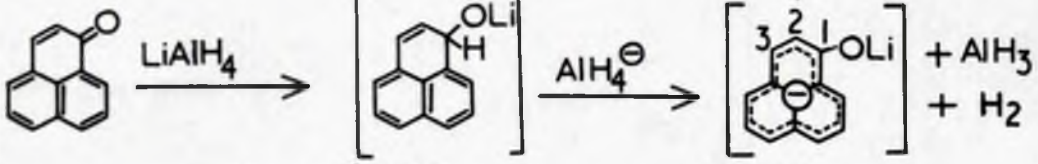
CXXXVII



CLXXXVIII

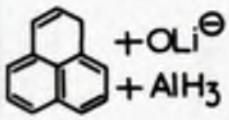


CLXXXIX

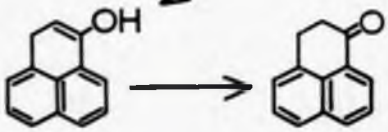


CXC

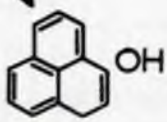
CXCI



XLVII



L



CXCII

The perinaphthenone must be formed during the oxygenation process, for a sample of the ether washing gave a strongly orange solution with concentrated hydrochloric acid after evaporation of the solvent. This indicates that the formation of the ketone is not the result of a thermal breakdown of the peroxide during sublimation and purification. The large quantity of perinaphthenone obtained from the ether washings is incompatible with the low solubility of the peroxide in ether.

Thermal decomposition of perinaphthyl peroxide yielded both perinaphthenone and peropyrene (LXVI). The ultra-violet absorption spectrum of peropyrene, prepared from perinaphthyl peroxide is shown on Plate VI. It is probable that perinaphthyl peroxide has the structure (CLXXXVII).

B. II. 4. The Perinaphthenylium Cation (CXVII).

The sequence of transformations, perinaphthene $\longrightarrow$ perinaphthenide $\longrightarrow$ perinaphthyl $\longrightarrow$ perinaphthenylium, was completed by the conversion of perinaphthyl to perinaphthenylium salts. The halogens, chlorine, bromine and iodine, all react with perinaphthyl to form products whose stabilities follow in the order iodide > bromide > chloride. The iodide is indefinitely stable when stored under nitrogen and

studies in this series have been confined to this compound. It is formed by the action of molecular iodine on an ethereal solution of perinaphthyl and exists as a violet-black solid possessing no definite melting point but decomposing on being heated to an orange yellow solid. It is insoluble in most organic solvents but dissolves to a small extent in nitromethane forming a green solution.

However, perinaphthenylium iodide is readily soluble in pyridine and related bases to form greenish-blue solutions which were shown to contain the perinaphthyl radical. The spectrum of the radical, prepared from perinaphthenylium iodide, in the region 750-460 mμ was identical with that of perinaphthyl prepared by oxygenation of the perinaphthenide anion (Plate IV). It showed the characteristic broad absorption maximum at 610-615 mμ, with a flat peak at 612-615 mμ. In boiling pyridine the iodide is rapidly converted to peropyrene.

These properties of the iodide (CXXXVI) are consistent with the view that in the solid state the bond between iodine and the perinaphthene moiety is ionic in character but that the molecule breaks down homolytically in pyridine to form perinaphthyl. This process of homolytic cleavage is assisted by the ability of pyridine to form a molecular complex with the iodine molecule[169]. A marked increase in the stability of the coloured entity is observed when perinaphthenylium iodide is added to nitromethane containing a Lewis acid e.g. aluminium chloride or stannic chloride. The resulting deep-green solutions are stable at the boiling point.

Conversion of the perinaphthyl radical to the perinaphthenylium cation has also been achieved by using as electron acceptor a metallic ion possessing a ready tendency to assume the metallic state. Thus, perinaphthyl and anhydrous silver perchlorate react in ether solution to form perinaphthenylium perchlorate (CXXXVII) and metallic silver. This compound has been synthesised by Pettit[170] by a process similar to that used by Dewar and Pettit[171] in the synthesis of tropylium salts. 3-Carbethoxy-7:8-cyclopropanoacenaphthene (CLXXXVIII; R= COOEt), formed by the addition of diazoacetic ester to acenaphthylene, was hydrolysed to the corresponding acid (CLXXXVIII; R= COOH) which in turn, was converted to the amine (CLXXXVIII; RNH_2) by a Curtius reaction; subsequent diazotisation in acid solution yielded 3-chloro-7:8-cyclopropanoacenaphthene (CLXXXVIII; R = Cl). Treatment of this compound with silver perchlorate in dry nitromethane at 70° for two hours yielded perinaphthenylium perchlorate (CXXXVII).

The perinaphthenylium cation, in the form of its perchlorate, has also been prepared by removal of a hydride ion from perinaphthene using triphenylmethyl perchlorate in glacial acetic acid solution (B, IV).

The properties of perinaphthenylium perchlorate prepared from perinaphthyl and by hydride ion removal from perinaphthene, were found to be in accord with those reported by Pettit[170]. Thus, the compound decomposes to a black tar on exposure to moist air. It is insoluble in all non-polar organic solvents but dissolves readily in

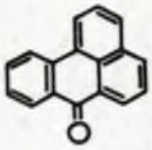
nitromethane giving green solutions. Both perinaphthenone and perinaphthene were obtained by decomposition of the perchlorate with water. As suggested by Pettit, these compounds probably arise by an irreversible disproportionation of the perinaphthenol (CLXXXIX) which is formed by hydrolysis of the salt. It is significant that an attempt by Bockelheide and Larrabee[105] to obtain (CLXXXIX) by the reduction of perinaphthenone with lithium aluminium hydride failed; the products isolated from this reaction were perinaphthen-1-one (65%), perinaphthene (14%) and phenolic material (13%). A plausible mechanism for the course of this reaction was advanced by Bockelheide and Larrabee. It was suggested that the initial product (CXC) may undergo further reaction to give either perinaphthene or a second intermediate (CXCI). On hydrolysis, the intermediate (CXCI) can yield either perinaphthenone (L), a phenol or perinaphthenol (CLXXXIX), depending on the position taken in the perinaphthene nucleus by the incoming proton. Addition of hydrogen at the 3-position would yield the enolic form of perinaphthen-1-one, addition at the 1-position would give perinaphthenol and addition at positions 4,6,7 or 9 would give a phenol (CXCIX and isomers). Postulation of (CXCI) as an intermediate is reasonable in view of the stability of the perinaphthenide anion.

B,II, 5. The Structure and Stability of the Perinaphthenylium Cation and the Perinaphthenide Anion.

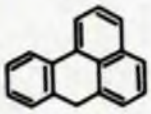
In a carbonium ion, the three bonds about the carbon atom carrying the positive charge are uniplanar and at an angle of 120° to one another. Hence, in the perinaphthenylium cation, the positive charge can be located on the central carbon atom without developing any steric strain in the molecule.

In a carbanion, on the other hand, the carbon atom bearing the negative charge must have a tetrahedral valency configuration because of the requirements for sp^3 hybridisation. Thus, an electron pair will not be localised on the central carbon atom of the perinaphthene nucleus since this would involve steric strain by nonplanarity. Hence, the perinaphthenide anion should involve resonance hybrids in which only the peripheral carbon atoms participate, in contrast to the perinaphthenylium cation in which the central carbon atom may also be involved.

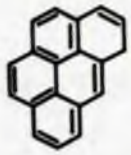
The ready conversion of anion to radical and the subsequent conversion of radical to cation would seem to indicate a corresponding increase in the order of stability of these entities. From a consideration of the stabilities of the aromatic compounds generally, greater stability seems to be associated with delocalised π-electron systems in which the number of mobile electrons and carbon atoms involved is the same. Thus, the greater stability of the cation is in accord with expectation.



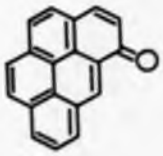
LXXIX



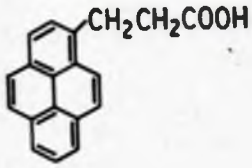
CXCIII



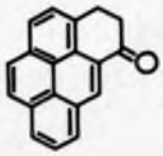
CXCIV



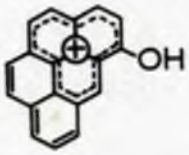
CXCV



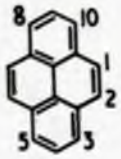
CXCVI



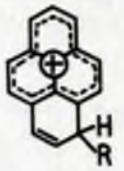
CXCVIII



CXCVII



CXCIX



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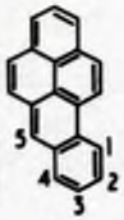
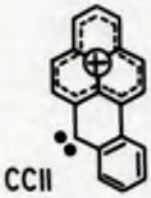


CCI



CCII

Perinaphthene is unique in the carbocyclic series in that significant delocalisation energy is invested in three distinct oxidation states, in direct contrast to cyclopentadiene and cycloheptatriene. Although only the transformation from anion to cation has so far been demonstrated, there appears to be no fundamental reason why the reverse transformation should not be possible. It is interesting to note that the mobile electron systems in the radical and cation do not conform to Hückel's Rule for aromaticity.

B. II.6. Other Hydrocarbons containing the Perinaphthene Nucleus.

The influence of the perinaphthene nucleus on the properties of some other ring systems in which it is incorporated, is worthy of mention.

Benzanthrone (LXXIX), or 2,3-benzperinaphthenone, the ketone derived from benzanthrene (LXXIII), is a compound of considerable interest in the dyestuffs industry and consequently much attention has been devoted to its synthesis and to a study of its properties. Like perinaphthenone, it is basic but the presence of a fused benzene ring results in a considerable decrease in the basicity and benzanthrone is soluble only in concentrated sulphuric acid. 1:4-Addition of Grignard reagents to benzanthrone has been demonstrated[120].

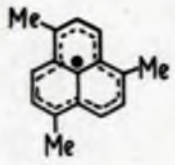
The most interesting property of benzanthrone involves its reduction with aluminium isopropoxide to give benzanthrene (CXCIII) in 50% yield[173], a process which parallels the action of lithium aluminium hydride on perinaphthenones. This conversion to benzanthrene is also effected by lithium aluminium hydride in the presence of aluminium chloride[173].

Benzanthrene has not been widely studied but it is oxidised by air to benzanthrone, again showing a parallel to perinaphthene. The capabilities of benzanthrene of forming a stable anion, radical and cation are presently being investigated.

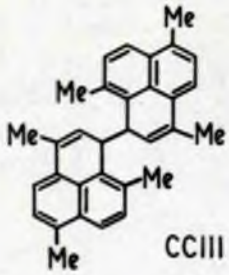
The influence of the perinaphthene ring system in the hydrocarbon (CXCIV) is also being investigated. As a preliminary to this study, the naphthoperinaphthenone (CXCV) was synthesised (i) by cyclisation of 3-pyrenylpropionic acid (CXCVI) using polyphosphoric acid and (ii) by the action of stannic chloride on the acid chloride of (CXCVI). This ketone dissolves reversibly in concentrated hydrochloric acid, forming the green cation (CXCVII) and shows infra-red carbonyl absorption at 1630 cm^{-1}, this abnormally low value being characteristic of the perinaphthenones (A,II,6). Doubtlessly, a better method for the preparation of (CXCV) involves cyclisation of 3-pyrenylpropionic acid to the naphthoperinaphthanone (CXCVIII) by the use of anhydrous hydrogen fluoride, followed by dehydrogenation to (CXCV) by the action of triphenylmethyl perchlorate (B,IV); this preparation is presently being investigated.

Pyrene (CXCIX), which may be regarded as derived by the peri fusion of a benzene ring to perinaphthene, is extremely stable and behaves as a benzenoid aromatic hydrocarbon. However, one aspect of its behaviour reflects the influence of the perinaphthene nucleus. Electrophilic substitution takes place at position 3 in the pyrene molecule and further substitution involves positions 6,8 and 10. Likewise, oxidation by chromic acid yields the 3,8 and 3,10 quinones (71). It has been suggested(174) that these positions owe their reactivity to the fact that they are situated at the terminal sites of a triene system. However, in view of the stability of the perinaphthenylium cation, it seems more reasonable to interpret these reactions in terms of a stabilised transition state involving delocalisation of a positive charge over the perinaphthene moiety (CC).

Similarly, in 3,4-benzpyrene (CCI), a molecule which is iso-electronic with indeno [2,1-a] -perinaphthene and which has been the subject of intense chemical study because of its carcinogenic nature, smooth electrophilic substitution has been shown to take place at position 5. This is due again to the stability of the reacting state (CCii), delocalisation of a positive charge over the perinaphthene moiety leading to ready reaction since the localisation of an electron pair at C_5 is thereby facilitated.

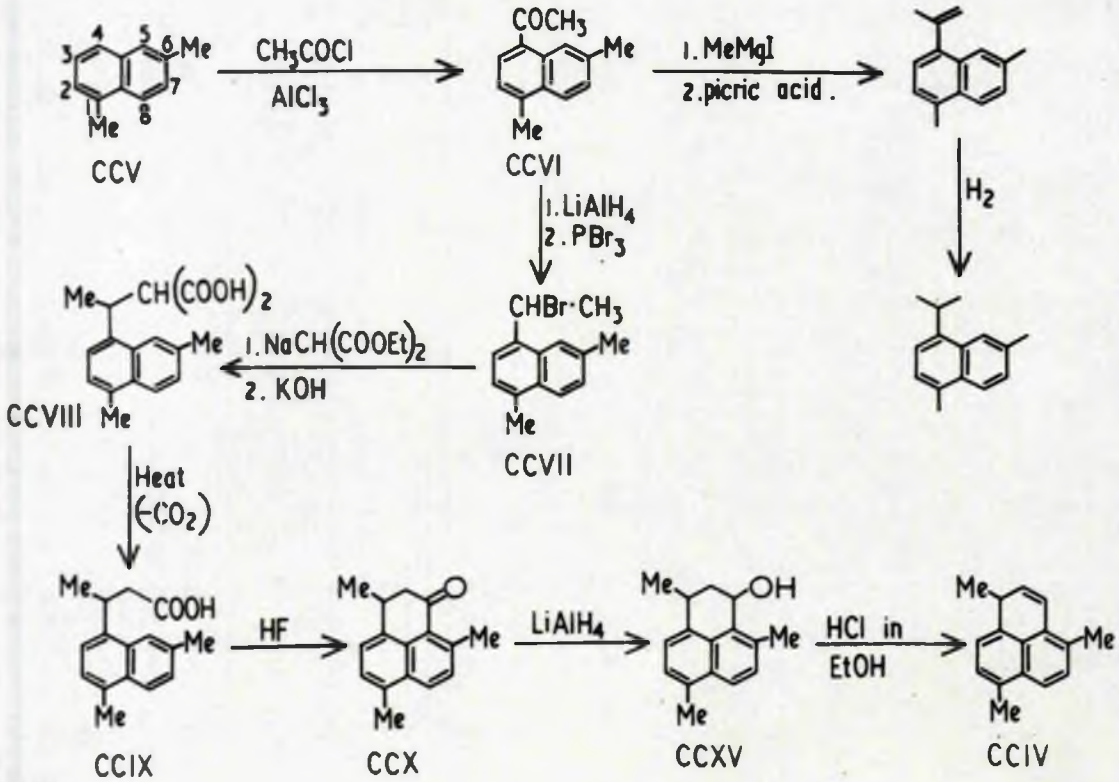


CXXXIV



CCIII

Synthesis of 1,4,7-Trimethylperinaphthene :–



CCV CCVI CCVII CCVIII CCIX CCX CCXV CCIV

B.III. The Radical and Cation derived from 1,4,7-Trimethylperinaphthene.

B. III. 1. Introduction.

The formation of peropyrene from perinaphthyl involves the eventual linking of two radicals, each through a pair of peri positions (B,II,3 (b).). A derivative, 1,4,7-trimethylperinaphthyl (CXXXIV), was therefore synthesised in which one position of each of the three pairs of peri positions is substituted by a methyl group. Aromatisation of the dimeric form (CCIII) is thus rendered impossible.

B. III.2. The Synthesis of 1,4,7-Trimethylperinaphthene.

1,4,7-Trimethylperinaphthene (CCIV) was synthesised from 1,6-dimethylnaphthalene (CCV) according to the scheme formulated opposite.

The position of substitution in 1,6-dimethylnaphthalene by acid chlorides has not been rigorously established although Cook[175] has shown that beyond any reasonable doubt, the 4 position is involved. Of the six positions available for attack by an electrophilic reagent, substitution at positions 2,5 or 7 would be most unlikely for steric reasons. Of the three remaining positions, attack by an electrophilic

reagent would be most favoured at carbon atom 4 since this position is para to an ortho-para directive methyl substituent and is an α position in the molecule. It has been shown[155] that Friedel-Crafts substitution of naphthalene in dichloroethane or methylene-chloride as solvent yields 98% of the α substituent and only 2% of the β substituent. Acetylation of 1,6-dimethylnaphthalene was therefore carried out in 1,2-dichloroethane and the product shown to be 4-acetyl-1,6-dimethylnaphthalene by conversion to cadalene (1,6-dimethyl-4-isopropylnaphthalene), which has been independently synthesised by several routes[176]-[181] and the structure of which is not in doubt. The dimethyl carbinol resulting from the reaction of acetyl-1,6-dimethylnaphthalene with methyl magnesium iodide was dehydrated using picric acid in ethanol solution[177], yielding the picrate of 1,6-dimethyl-4-isopropenylnaphthalene. Decomposition of the picrate and catalytic reduction of the ethylenic hydrocarbon yielded cadalene, characterised by formation of the picrate and trinitrobenzene complex.

With the structure of the acetyldimethylnaphthalene thus established, attempts were made to react it with bromoacetic ester in a Reformatski reaction under a variety of conditions. In all cases, unchanged ketone alone was obtained from the reaction mixtures. Many different experimental conditions have been recommended for the Reformatski reaction and inspection of the literature reveals that there is no uniformity as regards the procedures. Hence, four trial

runs were carried out under different conditions but in no case was any reaction product isolated. This lack of reactivity of the ketone in the Reformatski reaction is not unprecedented[182] and in many cases it has been shown that slight structural changes in the ketone are sufficient to affect the facility of the reaction for no readily apparent reasons.

This difficulty was obviated by a straightforward series of reactions involving reduction with lithium aluminium hydride of 4-acetyl-1,6-dimethylnaphthalene (CCVI) to methyl-1,6-dimethylnaphthyl-4 carbinol; the carbinol was converted by the action of phosphorus tribromide to 4(1-bromoethyl)-1,6-dimethylnaphthalene (CCVII). Condensation with malonic ester in the presence of sodium ethoxide, followed by alkaline hydrolysis of the product, led to 2-(1,6-dimethylnaphthyl-4)-1,1-dicarboxypropane (CCVIII). Decarboxylation of (CCVIII), followed by cyclisation of the product, β-(1,6-dimethylnaphthyl-4)-butyric acid (CCIX), using anhydrous liquid hydrogen fluoride, afforded 3,6,9-trimethylperinaphthan-1-one (CCX) in 38% overall yield from 1,6-dimethylnaphthalene.

Cyclisation of β-(1,6-dimethylnaphthyl-4) butyric acid (CCIX) can conceivably proceed to yield either one of the two products, the desired 3,6,9-trimethylperinaphthan-1-one (CCX) and the isomeric benzindanone (CCXI) or a mixture of both.

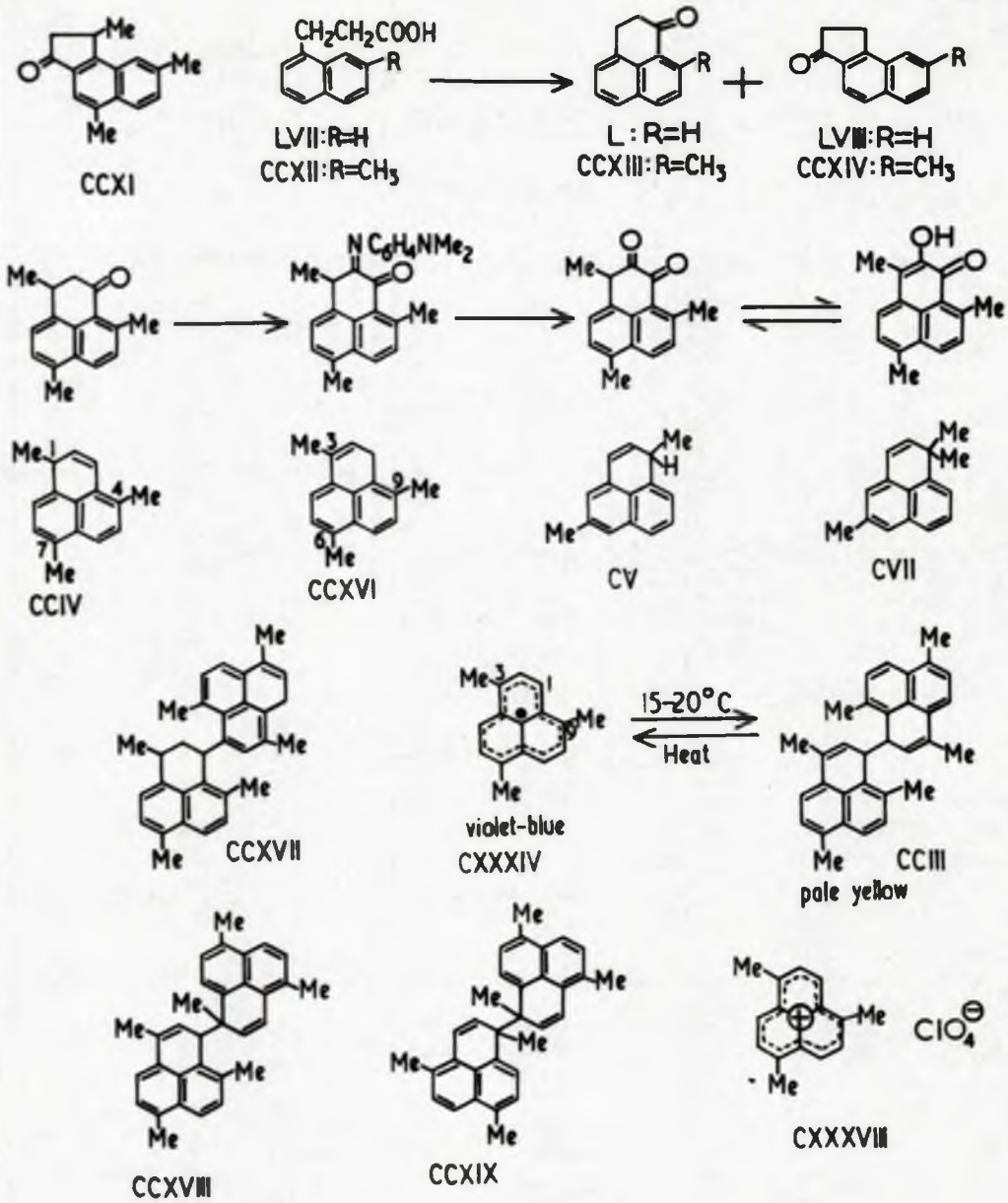
β-1-Naphthylpropionic acid (LVII), on treatment with stannic chloride[70] or anhydrous hydrogen fluoride[88], gives a small yield

of benzindanone (LVIII) along with perinaphthan-1-one (L) the primary product of peri cyclisation. Wenham and Whitehurst[133] cyclised β-7-methyl-1-naphthyl propionic acid (CCXII) using anhydrous hydrogen fluoride and obtained 9-methylperinaphthan-1-one (CCXIII) in high yield, accompanied by small amounts of 9-methylperinaphthenone. No evidence was found for the formation of the isomeric benzindanone (CCXIV) and it was concluded that the electron releasing properties of the methyl group far outweigh the steric effect.

In the present investigation, cyclisation of β-(1,6-dimethyl-naphthyl-4)-butyric acid (CCIX) using anhydrous hydrogen fluoride yielded a homogeneous product in 96% yield. The results obtained by Wenham and Whitehurst ruled out the possibility that this product could be the benzindanone (CCXI). Proof that the compound was 3,6,9-trimethylperinaphthan-1-one came from the following results.

(a) The infra-red spectrum of the compound showed carbonyl absorption bands at 1680 and 1672 cm^{-1}; the carbonyl absorption band of perinaphthan-1-one lies at 1670 cm^{-1}.[126] There was no peak at 1680 cm^{-1}, the carbonyl absorption frequency of 3,6,9-trimethylperinaphthenone, prepared later by dehydrogenation of 3,6,9-trimethylperinaphthan-1-one (C,XIII,3).

(b) The product of cyclisation of β-(1,6 dimethylnaphthyl-4) butyric acid was condensed with p-nitrosodimethylaniline in the presence of alkali and the resulting azomethine compound was hydrolysed using 5 N hydrochloric acid. The product of these reactions was a


CCXI
LVII:R=H
CCXII:R=CH3
L : R=H
CCXIII:R=CH3
LVIII:R=H
CCXIV:R=CH3
CCIV
CCXVI
CV
CVII
CCXVII
violet-blue
CXXXIV
15-20°C
Heat
CCIII
pale yellow
CCXVIII
CCXIX
CXXXVIII

hydroxyperinaphthenone derivative as evidenced from its characteristically low carbonyl absorption frequency in the infra-red (1638 cm^{-1}). The reaction sequence is formulated opposite. 2-Hydroxyperinaphthenone was prepared from perinaphthen-1-one by a similar reaction sequence for comparison purposes in the infra-red. The carbonyl absorption band was at 1618 cm^{-1}.

3,6,9-Trimethylperinaphthen-1-one (CCX) was reduced by lithium aluminium hydride to 3,6,9-trimethylperinaphthen-1-ol (CCXV) in almost quantitative yield. Dehydration of this alcohol using ethanolic hydrogen chloride yielded a pale yellow oil which could be induced to crystallise in only one instance. Recrystallisation of the solid caused large changes in its melting point. It was isolated as colourless needles, m.pt. 40-41° but after two recrystallisations, from light petroleum and a mixture of light petroleum and acetone, the melting points were 47-51° and 35-40°, respectively.

There are only two possible isomers of the symmetrically substituted trimethylperinaphthene; these are 1,4,7-trimethylperinaphthene (CCXV) and 3,6,9-trimethylperinaphthene (CCXVI). A rational explanation for the changes in the melting point is that the isomer (CCXV), the primary product of dehydration of 3,6,9-trimethylperinaphthen-1-ol (CCXV) was isolated from the reaction mixture. On recrystallisation, this was converted to the more stable, higher melting isomer (CCXVI), increased stability arising because of the presence of a more highly substituted double bond in the "peri" ring.

In no other dehydration experiment carried out using ethanolic hydrogen chloride could the pale yellow oil obtained be induced to crystallise. The oil was therefore purified by chromatography, followed by distillation and used as such in the reactions carried out on 1,4,7-trimethylperinaphthene. In view of the facile isomerisation of the perinaphthene nucleus, it seems probable that the above product is a mixture of 1,4,7-trimethylperinaphthene (CCIV) and 3,6,9-trimethylperinaphthene (CCXVI); it should be borne in mind that in the compound hereafter referred to as 1,4,7-trimethylperinaphthene, the position of the peri double bond is uncertain. 1,4,7-Trimethylperinaphthene was invariably accompanied by a small amount of a high melting crystalline product in these dehydrations. This was the only product which could be isolated in attempts to dehydrate 3,6,9-trimethylperinaphthan-1-ol using phosphorus pentoxide in benzene. The high melting point, and the analytical figures, indicate that this compound is a polyhydroditrimethylperinaphthan-1-yl with a structure similar to (CCXVII).

Attempts to oxidise 1,4,7-trimethylperinaphthene to the corresponding substituted perinaphthenones using (i) chromic anhydride in acetic acid (ii) sodium dichromate in acetic acid and (iii) p-nitrosodimethylaniline in ethanol were fruitless, tarry products being produced in each case, from which nothing useful could be obtained.

B, III, 5. The Preparation and Properties of 1,4,7-Trimethylperinaphthyl

1,4,7-Trimethylperinaphthyl could not be prepared by the action of oxygen on a solution of 1,4,7-trimethylperinaphthene in ethanolic ether containing potassium methoxide, owing to the decreased acidity of the hydrocarbon as compared with perinaphthene. This decrease in acidity which is a result of the presence of three electron releasing substituents in the molecule, causes a suppression in the ionization of the hydrocarbon to such an extent that, under the reaction conditions, the equilibrium concentration of the 1,4,7-trimethylperinaphthenide anion is inadequately low. Similarly, treatment of 1,4,7-trimethylperinaphthene with butyl lithium or with ethyl magnesium bromide resulted in the recovery of unchanged hydrocarbon.

In this connection, it is pertinent to refer again to the methylation of 1,5-dimethylperinaphthene (CV)[152]. Treatment of this compound with phenyl lithium and methyl iodide yielded a trimethylperinaphthene which, because of its failure to undergo further methylation on treatment with phenyl lithium and methyl iodide was formulated as 1,1,5-trimethylperinaphthene (CVII). Resistance to anion formation was considered due to the presence of a gem dimethyl grouping. This conclusion was drawn without the support of any degradative or synthetic evidence.

In the light of the unsuccessful attempts to form the anion of 1,4,7-trimethylperinaphthene, it would seem that the failure to

methylate "1,1,5-trimethylperinaphthene" is not necessarily due to the presence of a gem dimethyl grouping. There is no conclusive reason why methylation of 1,5-dimethylperinaphthene should occur at position 1 in preference to positions 3,4,6,7 or 9, and the structure of Boekelheide's and Coldman's trimethylperinaphthene must accordingly remain uncertain. The presence or otherwise of a gem dimethyl grouping could be indicated by treatment of the compound with a solution of triphenylmethyl perchlorate in glacial acetic acid (B,IV). Inability to undergo cation formation would indicate the presence of a gem dimethyl grouping while the absence of such a grouping would be shown by the formation of a stable cation.

The only means of formation of 1,4,7-trimethylperinaphthyl was by a free radical abstraction of hydrogen from the hydrocarbon by the use of N-bromosuccinimide; the radical was obtained as a violet-blue entity from this reaction. It is noteworthy that, after chromatography, the solution containing the radical was pale yellow in colour, the violet-blue colour appearing only when the solution was warmed. The intensity of the blue colour increased as the temperature of the solution was raised and the radical was stable in the absence of oxygen in α-methylnaphthalene at its boiling point (240°). On cooling to room temperature, the colour of the methylnaphthalene solution reverted slowly to a pale greenish yellow. A consideration of this result leads to the conclusion that an equilibrium exists between radical (CXXXIV) and dimer (CCIII), the effect of heat being

to shift the equilibrium in favour of the radical.

As in the unsubstituted perinaphthyl radical, dimerisation of (CCXXXIV) can occur only through the peri positions 1,3,4,6,7 and 9. In this case, there are three distinct dimeric forms to which the radical can conceivably give rise; these are (CCXXX), (CCXXXI) and (CCXXX). For steric reasons, (CCXXX) is considered to be the most probable structure for the dimeric form of 1,4,7-trimethylperinaphthyl. In this case of an equilibrium between radical and dimer, however, it appears that the dimeric form is energetically less favoured than the radical (CCXXXIV).

The thermally controlled equilibrium which exists between 1,4,7-trimethylperinaphthyl and its dimeric form prevented any attempt being made to obtain an accurate record of the ultra-violet absorption properties of the radical.

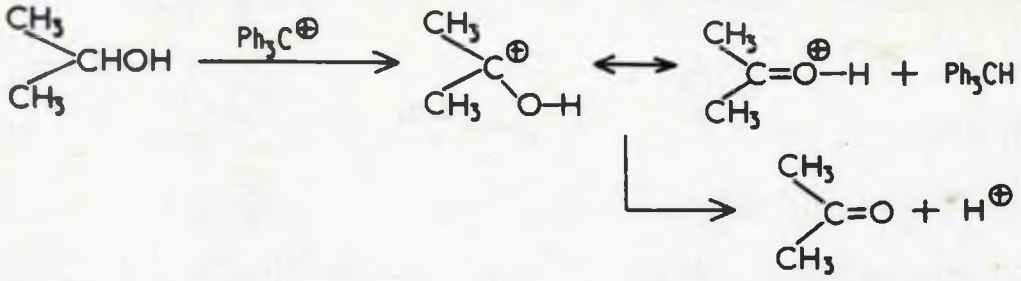
The radical was, however, reacted with molecular iodine. This reaction was carried out by treating an ethereal solution of the blue radical, after rapid chromatography, with a solution of iodine in benzene with the minimum of delay. The black precipitate obtained gave analytical figures corresponding to those required by a compound of molecular formula $C_{16}H_{15}I_2$. On this evidence, and in view of the stability of 1,4,7-trimethylperinaphthyl, it is considered that this compound is a radical: molecular iodine complex.

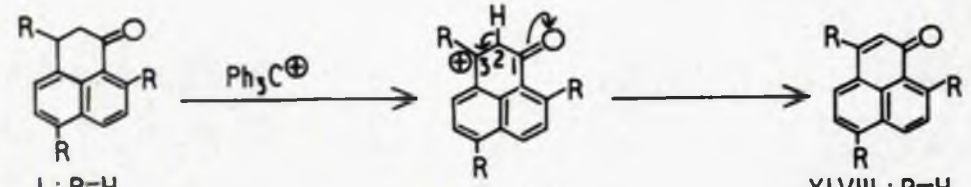
B,III,4. The Trimethylperinaphthenylium Cation.

1,4,7-Trimethylperinaphthenylium perchlorate (CXXXVIII) was isolated as stable copper coloured needles by treatment of 1,4,7-trimethylperinaphthene with a solution of triphenylmethyl perchlorate in glacial acetic acid. The rationale of this procedure is discussed in the following section.

As has been stated above, the suppressed acidity of 1,4,7-trimethylperinaphthene compared with perinaphthene is to be traced to the electron releasing effect of the three methyl substituents. This same effect causes an increased stabilisation of the positive charge in the 1,4,7-trimethylperinaphthenylium cation to such an extent that this cation parallels the tropylium cation in its stability, these being the only known cations which are stable in the presence of water.

In the presence of strong alkali, however, it can be foreseen that decomposition of trimethylperinaphthenylium perchlorate will take place yielding 3,6,9-trimethylperinaphthenone and 1,4,7-trimethylperinaphthene in the same manner as perinaphthenylium perchlorate disproportionates in the presence of water yielding the corresponding unsubstituted compounds (B,II,4). Time, however, precluded any experiments along these lines utilising trimethyl-perinaphthenylium perchlorate.

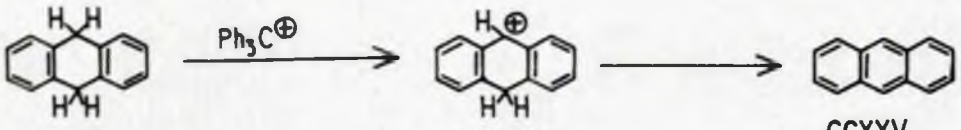




L : R=H
CCX : R=CH3

CCXXI : R=H
CCXXII : R=CH3

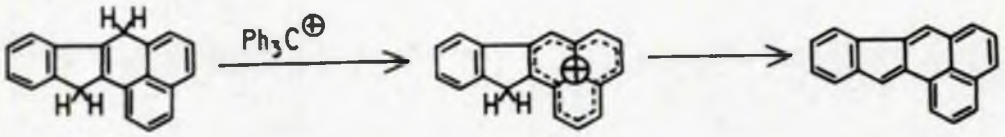
XLVIII : R=H
CCXX : R=CH3



CCXXIII

CCXXIV

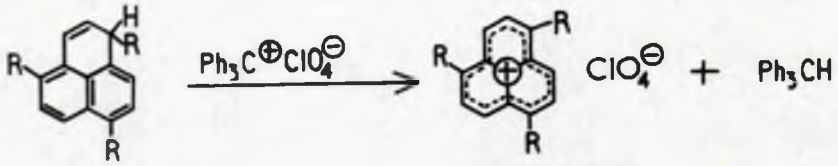
CCXXV



CLXXX

CXXV

CXXIV



XLVII : R=H
CCIV : R=CH3

CXXXVII : R=H
CXXXVIII : R=CH3

B.IV. Dehydrogenation by hydride transfer followed by proton elimination using the triphenylmethyl carbonium ion.

By a hydride transfer is meant the acquisition, in a single step, of a proton and two electrons by one electrophilic centre at the expense of another centre, either in the same or in a different molecule[184].

Bartlett and McCollum[184] have proved kinetically that the triphenylmethyl carbonium ion, generated in solution, is responsible for the oxidation of alcohols to carbonyl compounds. The reaction between isopropyl alcohol and triphenylcarbinol was studied in sulphuric acid-water mixtures and was found to be of the second order. The reaction proceeds by the initial removal of a hydride ion from the alcohol by the strongly electrophilic triphenylmethyl carbonium ion, followed by the loss of a proton from the oxygen atom of the substrate; the reaction is formulated opposite.

The possibility of effecting dehydrogenations by this process, involving hydride transfer from the substrate to the electrophilic reagent followed by proton elimination from the resulting carbonium ion as the secondary step, was investigated. The following two factors assume importance in the hydride transfer reaction:-

(i) The electrophilic nature of the reagent. Other factors being constant, the more stable carbonium ions would be expected to be less reactive. This is borne out by experiments using tri-p-anisyl-

carbinol which was found to have a dissociation constant greater by 7.36 logarithmic units than that of triphenylcarbinol. This stable cation was quite unreactive in hydride transfer with isopropyl alcohol, being only one thousandth as fast as the triphenylmethyl cation[184]. The triphenylmethyl carbonium ion was therefore selected as the electrophile in dehydrogenation reactions and was found to serve satisfactorily in this capacity.

(ii) Structural features in the substrate which are capable of stabilising the carbonium ion formed by hydride transfer.

The success of the secondary step depends on the presence in the intermediate carbonium ion of a hydrogen atom which is capable of ready loss as a proton.

The following are examples of dehydrogenations carried out by hydride-proton elimination. Triphenylmethyl perchlorate was used in all cases as the dehydrogenating reagent and acetic acid as the reaction solvent.

Perinaphthenone (L) and 3,6,9-trimethylperinaphthenone (CCK) were converted in a few minutes at the boiling point of acetic acid to perinaphthenone (CLVIII) and 3,6,9-trimethylperinaphthenone (CCKX), respectively. The driving force for the initial hydride transfer is derived from (i) the strongly electrophilic nature of the triphenylmethyl cation and (ii) the resonance stabilisation of the resulting cations (CCKXI) and (CCKXII). Completion of the reaction by the loss of a proton from C_2 is aided by the electron attracting nature of the

carbonyl group and by the resonance stabilisation of the products (XLVIII) and (CCXX). In each case, triphenylmethane was obtained in high yield.

9,10-Dihydroanthracene (CCXXIII) carries the necessary structural features governing the success of this reaction. These are (i) the ability to form a resonance stabilised carbonium ion (CCXXIV), and (ii) a stable dehydrogenation product which provides the driving force for the secondary step. Anthracene (CCXXV) was formed in 90% yield by dehydrogenation of 9:10-dihydroanthracene.

When this method was applied to dihydroindeno [2,1-a-]-perinaphthene (CLXXX), dehydrogenation to indeno [2,1-a]-perinaphthene (CXXIV) occurred at room temperature. This reaction proceeds by the initial formation of the indeno [2,1-a]-perinaphthenylium cation (CXXV) which readily loses a proton with formation of the fully conjugated aromatic hydrocarbon.

In certain cases, the intermediate carbonium ion resulting from the initial step may be unusually stable and capable of isolation as its salts. Thus, tropylidenes readily undergo hydride transfer reactions with triphenylmethyl perchlorate or triphenylmethyl fluoroborate forming tropylium salts[186]. Perinaphthene (XLVII) and 1,4,7-trimethylperinaphthene (CCIV) likewise form perinaphthenylium perchlorate (CXXXVII) and 1,4,7-trimethyl-perinaphthenylium perchlorate (CXXXVIII) on treatment with triphenylmethyl perchlorate in acetic acid at room temperature

(C,VII,3) and (C,XII,3) .

Further studies of dehydrogenation reactions by hydride exchange followed by proton elimination are in progress.

NOTES.

Infra-red spectral measurements on the following compounds were carried out by M.St.C.Flett (I.C.I., Manchester):- 2:3-cyclopentanoperinaphthenone (CXLII), the mixture of α-naphthoylcyclopent-1-ene (CXXXIX) and 3:3-cyclopentanoperinaphthan-1-one (CXL), and 1-1'-diperinaphthan-1-ol (CLXVI). The remainder of the infra-red measurements were carried out by the author on a Grubb-Parsons G.S. 2 A Double Beam instrument. As only certain absorption maxima are of relevance, the entire spectrographs have not been reproduced in this work.

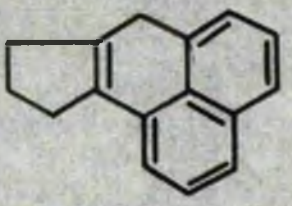
The ultra-violet and visible absorption spectra were measured on a "Unicam" S.P. instrument.

The melting-points were determined on a Kofler-type heating stage.

Micro-analyses were conducted by Drs. Weiler and Strauss, Oxford.

The terms light petroleum and petroleum ether refer to those solvents commonly designated as petroleum ether (b.pt. 40-60°) and petroleum ether (b.pt. 60-80°).

C,I. The Synthesis of 2:3-cyclopentenoperinaphthene. (CXLIII).

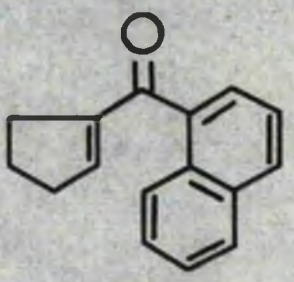


(CXLIII)

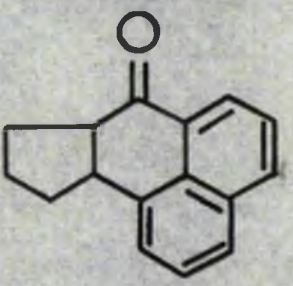
C,I,1. Cyclopentene-1-carboxylic acid chloride.

Cyclopentene-1-carboxylic acid, m.pt. 120-121°C, was prepared from cyclopentanone by the method of Cook and Linstead[136] and using the modification described by Baker and Leeds[137]. The acid chloride, b.pt. 65°C/16 m.m. (lit 65-67°C/16 m.m.[137] and 179-180°C/758 m.m.[138]) was formed in 90% yield by the method of Baker and Jones[137].

C,I,2. The mixture of α-naphthoylcyclopent-1-ene (CXXXIX) and 2:3-cyclopentenoperinaphthen-1-one (CXL).



(CXXXIX)



(CXL)

To a boiling solution of cyclopentene-1-carboxylic acid chloride (11.0 gms) and powdered, anhydrous aluminium chloride (11.25 gms) in

dichloromethane (30 mls) was added a solution of naphthalene (10.6 gms) in dichloromethane (30 mls) over a period of twenty minutes with stirring. When addition was complete, the solution was boiled under reflux for a further thirty minutes and, after cooling, was hydrolysed by pouring on to ice (150 gms) and concentrated hydrochloric acid (8 mls). The organic layer was separated, washed in turn with water (2 x 150 mls), saturated sodium bicarbonate solution (200 mls) and water (2 x 150 mls) and dried (K_2CO_3) and the solvent removed from the filtered solution. Test tube scale extraction of a benzene solution of the residual brown oil with concentrated hydrochloric acid showed the absence of 2:5-geolgeranenaperinaphthanone (CXLII). Distillation of the brown oil yielded unchanged naphthalene (9 gms) followed by a pale yellow oil (0.70 gm, 5% based on the acid chloride used), b.pt. 146-148°C /0.6 m.m.

Analysis: Found C 85.94 H 6.36%

$C_{15}H_{16}O$ requires C 86.44 H 6.36%

When this reaction was carried out at room temperature using 1,2-dichloroethane as solvent, the yield was unchanged.

The 2,4-dinitrophenylhydrazone was prepared by dissolving the product (772 mgms) and 2,4-dinitrophenylhydrazine (600 mgms) in ethanol (11 mls) containing concentrated hydrochloric acid (0.2 ml) and boiling the solution under reflux for twenty minutes. The precipitated dinitrophenylhydrazone (1 gm) was collected from the cooled solution and, after successive recrystallisations from glacial acetic

acid and dimethylformamide, it formed red needles, m.pt. 230-235°C with decomposition.

Analysis: Found C 65.57 H 4.62 N 14.15%

$C_{22}H_{18}N_4O_4$ requires C 65.66 H 4.51 N 15.93%

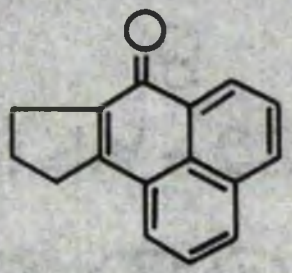
The ketonic product appeared to be a mixture of α-naphthoylcyclopent-1-ene (CXXXIX) and 2:3-cyclopentenoperinaphthen-1-one (CXL) as evidenced by a study of the infra-red spectrum which showed carbonyl absorption bands at 1647 cm^{-1} (α,β-unsaturated carbonyl) and at 1701 cm^{-1} (six-membered ring carbonyl).

C.I.5. Oxidation of the above mixture.

To a solution of the yellow oil (1.4 gms) in glacial acetic acid (10 mls) was added a solution of $Na_2Cr_2O_7.1OH_2O$ (14 gms) in acetic acid (30 mls) and the mixture boiled under reflux for two hours. After cooling, it was poured into water (300 mls) and the organic material was extracted into benzene. The benzene solution was washed with water (5 x 250 mls), dried (Na_2SO_4) and the solvent removed, leaving a pale yellow solid (700 mgms). This was sublimed at 150°C/0.5 m.m. yielding a pale yellow tacky solid, soluble in 5% sodium hydroxide solution and reprecipitated by acid, and melting over a range between 40 and 90°C. After one further sublimation, followed by recrystallisation from aqueous ethanol, the melting range was unchanged.

The use of potassium permanganate in acetone as oxidising agent yielded a product which melted over a similar range.

C.I.4. Attempted conversion of the mixture of (CXXXIX) and (CXL) to 3:5-cyclopentenoperinaphthenone (CXLII).



(CXLII)

The following sets of conditions were used in turn:

(i) A solution of the ketonic mixture (1.87 gms; 1 mol) in benzene (35 mls) was boiled under reflux with powdered, anhydrous aluminium chloride (5.37 gms; 3 mols) for ninety minutes, following the procedure of Baker and Jones[157] for the conversion of 1-benzoylcyclopentene to 1,2,3,8,9,10 - hexahydro - 8-ketocyclopenta a indene.

(ii) The oil (1.65 gms) was heated at 180° for forty-five minutes with 20% palladium on charcoal (0.33 gms) and then the organic material was extracted into methanol (cf. Loudon and Ramden[85] for the dehydrogenation of 9-hydroxyperinaphthan-1-one).

(iii) A solution of the oil (1.05 gms; 1 mol) in 1,2-dichloroethane (15 mls) was boiled under reflux with powdered, anhydrous aluminium chloride (2 gms; 2 mols) for one hour.

(iv) A solution of the oil (1 gm) in dichloromethane (15 mls) was boiled

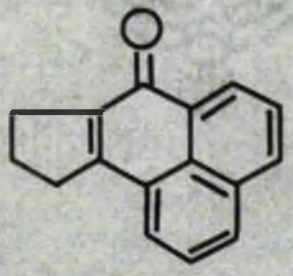
under reflux with powdered, anhydrous aluminium chloride (2 gms) for 3½ hours.

(v) A solution of the ketonic mixture (1.48 gms; 1 mol) in 1,2-dichloroethane (35 mls) was boiled under reflux with stannic chloride (2.34 mls; 3 mols) for one hour.

(vi) The oil (0.5 gm) was added to a melt prepared from sodium chloride (2 gms) and aluminium chloride (7.5 gms). The mixture was warmed at 130-150° for one hour and then at 200° for thirty minutes, cooled, and poured into water. This parallels the procedure described by Fieser and Hershberg[78] for the conversion of 8-benzoylperinaphthene to 2-1'-trimethylene-1,9-benzanthrone-10.

In no case was any more than a negligible amount of the desired product obtained on working up the reaction mixtures.

C,I,3. 2:3-cyclopentenoperinaphthenone (CXLII).



(CXLII)

To an ice-cooled solution of cyclopentene-1-carboxylic acid chloride (27.1 gms; 1 mol) and naphthalene (27 gms; 1 mol) in 1,2-dichloroethane (100 mls) contained in a 500 ml. three necked flask fitted with a mercury sealed stirrer, a reflux condenser and a

calcium chloride tube, was added powdered, anhydrous aluminium chloride (66.5 gms; 5 mols) over a period of thirty minutes with stirring. The solution was then stirred for two hours, allowed to stand overnight at room temperature and, finally, boiled under reflux for one hour. The cooled solution was poured on to crushed ice (250 gms) and concentrated hydrochloric acid (25 mls). The organic layer was separated, washed successively with water (2 x 300 mls), 5% sodium hydroxide solution (2 x 300 mls) and water (2 x 300 mls) and dried (K_2CO_3). The dichloroethane was evaporated and the residual brown oil was dissolved in benzene (750 mls). The benzene solution was extracted with concentrated hydrochloric acid until the acid extracts were only pale yellow in colour (4 x 250 mls).

The combined hydrochloric acid extracts were washed once with benzene (250 mls) then filtered through a sintered glass funnel and poured into water (4 litres). The precipitated yellow oil was extracted with some difficulty into benzene (1½ litres) and the benzene solution was washed with water (2 x 500 mls), saturated sodium bicarbonate solution (5 x 500 mls) and water (2 x 500 mls) and dried (Na_2SO_4). Solvent was removed by distillation, leaving a brown solid. A portion was sublimed at reduced pressure and the remainder was recrystallised from methanol with charcoal screening.

The sublimed sample formed yellow prisms, m.pt. 143-146°C. After one further sublimation at 150°C / 0.2 m.m., followed by two recrystallisations from a mixture of petroleum ether and benzene (1:1),

the melting point was constant at 147-148°C.

Analysis: Found C 87.70 H 5.55%

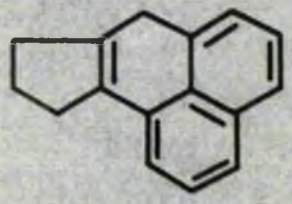
$C_{16}H_{12}O$ requires C 87.24 H 5.49%

The sample which was recrystallised from methanol formed dark yellow prisms, m.pt. 142.5 - 145°C. Further purification by distillation yielded a pale yellow oil, b.pt. 202-204°C / 1 m.m., which crystallised from a mixture of benzene and petroleum ether as yellow prisms, m.pt. 147-148°C. The total yield of pure 2:3-cyclopentenoquinonaphthenone was 7 gms (15%). The carbonyl absorption frequency in the infra-red was at 1634 cm^{-1}.

The benzene solution which had been extracted with concentrated hydrochloric acid was filtered through a sintered glass funnel, washed with water (2 x 500 mls), saturated sodium bicarbonate solution (2 x 500 mls), water (500 mls) and dried (Na_2SO_4). The solvent was removed and the dark brown residue was distilled affording 15 mls of a pale yellow oil, b.pt. 170-180°C / 1 m.m. There was a considerable tarry residue in the distilling flask. Redistillation through a short Vigreux column yielded a pale yellow oil (12.2 gms; 27%), b.pt. 144-152°C / 0.6 m.m.

This compound afforded a 2,4-dinitrophenylhydrazone, which, after recrystallisation from glacial acetic acid, formed red needles, m.pt. 322-325°C with decomposition. On admixture with a sample of the 2,4-dinitrophenylhydrazone obtained in (C,I,2), the melting point was not depressed.

C,I,6. Reduction of 2:3-cyclopentenoperinaphthenone with lithium aluminium hydride: First experiment.



(CXLIII)

The reduction was carried out in a three-necked flask fitted with a double surface condenser carrying a nitrogen-inlet tube at the upper end and a Soxhlet extractor and condenser. The third neck, used for the introduction of solid hydride and tetrahydrofuran, was kept closed during reaction.

Lithium aluminium hydride (0.7 gm) and dry tetrahydrofuran (250 mls) were placed in the flask. The apparatus was flushed out with a stream of dry nitrogen. When all the air had been replaced by nitrogen, extraction was begun, a slight positive pressure of nitrogen being maintained.

2:3-cyclopentenoperinaphthenone (2.15 gms) was extracted into the solution by gentle boiling of the solvent under reflux. Extraction was complete in 1½ hours and the mixture was boiled under reflux for a further thirty minutes. After cooling, it was poured on to a mixture of crushed ice (500 gms), concentrated hydrochloric acid (50 mls) and ether (500 mls). The organic layer was separated and the aqueous layer extracted with ether (2 x 200 mls) and discarded. The ether solutions were washed successively with water (2 x 500 mls), 5% sodium

hydroxide solution (2 x 250 mls) and water (2 x 250 mls), and dried (Na_2SO_4).

Solvent was removed from the pale yellow ether solution and the residual oil was dissolved in a mixture of light petroleum and benzene (4:1) before chromatography on a column of alumina (12 x 2.5 cm). Two fractions were collected.

Removal of solvent from the first fraction (600 mls, colourless; eluant, light petroleum) gave a colourless oil (956 mgms; 55% based on the ketone used), which did not crystallise. A solution of the oil (226 mgms) in ethanol (1 ml) treated with a solution of trinitrobenzene (234 mgms) in ethanol (5 mls) gave a trinitrobenzene complex which, after two crystallisations from ethanol, formed dark red needles, m.pt. 130-133°. The melting point of the trinitrobenzene complex of, formally, 8:9-cyclopentenoperinaphthene (C,I,8), prepared by a similar reduction of 8:9-cyclopentenoperinaphthenone, was 130-135°C. The mixed melting point was 129-136°C.

The remainder of the hydrocarbon (730 mgms), dissolved in a mixture of ethanol (4 mls) and benzene (1 ml) was added to a solution of picric acid (750 mgms) in ethanol (10 mls) containing one drop of concentrated hydrochloric acid. The picrate formed dark red prisms (900 mgms), m.pt. 105-109°C with decomposition. Attempts to recrystallise this compound led to decomposition.

Removal of solvent from the second chromatographic fraction (500 mls, yellow; eluants, benzene and a mixture of benzene and ether)

gave a yellow solid which, after sublimation at 130-150°C / 0.5 m.m. followed by recrystallisation from petroleum ether, yielded unchanged ketone (940 mgms), m.pt. 145-146°C.

C,I,7. Reduction of 2:3-cyclopentenoperinaphthenone with lithium aluminium hydride: Second experiment.

2:3-cyclopentenoperinaphthenone (1.44 gms) was extracted into a refluxing solution of lithium aluminium hydride (470 mgms) in anhydrous ether after the air had been swept out of the apparatus by dry nitrogen. A slight positive pressure of nitrogen was maintained in the reaction flask during extraction which was complete after five hours. The cooled mixture was hydrolysed by pouring it on to a mixture of crushed ice (150 gms) and dilute hydrochloric acid (150 mls). The organic layer was separated and the aqueous acid layer washed with a fresh portion of ether (200 mls) and discarded. The ether solutions were washed successively with water (2 x 200 mls), 5% sodium hydroxide solution (150 mls) and water (2 x 150 mls), and dried (Na_2SO_4). The solvent was evaporated and the residual pale yellow oil was dissolved in a mixture of light petroleum (15 mls) and benzene (5 mls) prior to chromatography on a column of alumina (12 x 2.5 cms).

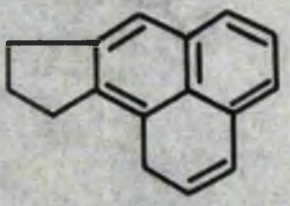
The column was developed and eluted with light petroleum until no further material came through. Thereafter, a yellow substance, held at the top of the column, was eluted with a mixture of ether and benzene

(1:1).

The light petroleum eluate (300 mls) was concentrated to a volume of 2 mls. On cooling to -70°, a very pale yellow solid crystallised. One crystal was removed as a seed and the solid was redissolved in light petroleum (1 ml). The solution was cooled and seeded and crystallisation allowed to proceed. The hydrocarbon was obtained as colourless prisms (226 mgs; 53% based on ketone used), which after one further crystallisation from light petroleum, melted over a range between 65 and 75°C (bulk 70-75°).

Removal of the solvents from the yellow benzene/ether eluate (300 mls) left a yellow solid which after sublimation at 130-150° / 0.5 m.m. followed by recrystallisation from petroleum ether yielded unchanged ketone (980 mgms), m.pt. 145-147°C.

C,I,8. Reduction of 8:9-cyclopentenoperinaphthenone with lithium aluminium hydride.



(CXLIX)

8:9-cyclopentenoperinaphthenone[129] (305 mgms) was extracted into a solution of lithium aluminium hydride (165 mgms) in anhydrous ether (250 mls) boiling under reflux in a flask filled with dry nitrogen. The extraction was continued for one hour under a slight

positive pressure of nitrogen; the cooled mixture was poured on to a mixture of crushed ice (150 gms) and dilute hydrochloric acid (100 mls) and the organic layer separated. The aqueous acid layer was washed with a fresh portion of ether (150 mls) and discarded. The combined ether solutions were washed with water (2 x 200 mls), 5% sodium hydroxide solution (150 mls) and water (200 mls) and dried (Na_2SO_4) before removal of the solvent by distillation. The residual pale yellow oil, dissolved in a mixture of light petroleum (10 mls) and benzene (4 mls), was chromatographed on a column of alumina (12 x 2.5 cm). The column was developed and eluted with light petroleum (300 mls). The strong yellow band held at the top of the column was then washed through with ether.

The light petroleum eluates, after concentration to a volume of 30 mls, were again filtered through a short column of alumina (4 x 2.7 cms) and the hydrocarbon was eluted with light petroleum. The hydrocarbon crystallised from the concentrated eluates (2 mls) as colourless prisms (250 mgms; 5%), m pt. 71-81°C (bulk 77-81°C). The melting point was unchanged after one recrystallisation from light petroleum. The melting point on admixture with the product obtained by the reduction of 2,3-cyclopentenoperinaphthenone was 71-81°C.

The trinitrobenzene complex, prepared in ethanol, formed orange needles, m.pt. 130-135°C with decomposition. The melting point was unchanged after one recrystallisation.

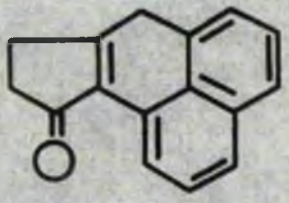
C,I,9. Oxidation of 2:3-cyclopentenoperinaphthene with sodium dichromate.

A solution of $Na_2Cr_2O_7.2H_2O$ (96 mgms; 60% excess) in acetic acid (10 mls) was added to a solution of 2:3-cyclopentenoperinaphthene (65 mgms) in glacial acetic acid (5 mls). The resulting solution was boiled under reflux for thirty minutes, during which time the colour changed from red to green. The cooled solution was poured into water (50 mls) and the aqueous mixture was extracted with benzene (2 x 75 mls). The aqueous phase was discarded and the combined benzene extracts were washed with water (2 x 50 mls), then filtered and extracted with concentrated hydrochloric acid until the acid layer was colourless (5 x 25 ml portions); the benzene layer was then discarded. The acid extracts were poured into water (250 mls) and the precipitated oil was taken into benzene (2 x 75 mls). The benzene solution was washed successively with water (2 x 50 mls), saturated sodium bicarbonate solution (2 x 50 mls) and water (50 mls) and dried (Na_2SO_4) before removal of the solvent by distillation. The residual yellow solid was sublimed at 170°C /0.5 m.m. Recrystallisation of the sublimate from petroleum ether yielded yellow needles (25 mgms; 37%) which melted over a range between 93° and 137°C. After a further recrystallisation from petroleum ether, the melting range was 100-142°C.

C,I,10. Oxidation of 8:9-cyclopentenoperinaphthene with sodium dichromate.

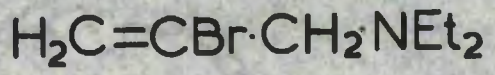
A solution of $Na_2Cr_2O_7.2H_2O$ (430 mgms; 132% excess) in acetic acid (10 mls) was added to a solution of 8:9-cyclopentenoperinaphthene (215 mgms) in glacial acetic acid (15 mls) and the resulting solution was boiled under reflux for thirty minutes. The reaction mixture was worked up as in (C,I,9) and purification by sublimation at 170°C / 0.5 m.m., followed by recrystallisation from a mixture of benzene and petroleum ether, yielded yellow needles (95 mgms; 41%) melting over a range between 105° and 140°C.

C.II. The Projected Synthesis of 10-Oxo-7,8,9,10-Tetrahydrocyclopenta[a]perinaphthene (CLV)



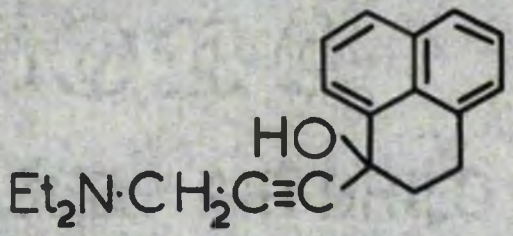
(CLV)

C.II.1. 2-Bromo-3-diethylaminoprop-1-ene.



This compound was prepared by the method described by Parcell and Pollard[189].

C.II.2. 1-(3-Diethylaminoprop-1-ynyl)-perinaphthen-1-ol.



The reaction was carried out in a one-litre three-necked flask cooled to -40° in a bath of solid carbon dioxide in ethanol. The first neck carried an inlet tube for the passage of nitrogen, the second a mercury sealed stirrer and the third a two-way adaptor carrying a loosely packed soda-lime tube and a 100-ml dropping funnel fitted with a calcium chloride tube.

Liquid ammonia (400 mls) was introduced into the flask and the

air swept out with a stream of dry nitrogen. When all the air had been displaced, stirring was started and lithium (0.1 gm) was added to the liquid ammonia; it dissolved to give a blue solution which on addition of hydrated ferric nitrate (0.05 gm) turned grey. The remainder of the lithium (2.1 gms) was then added in small pieces over a period of fifteen minutes, while a slow stream of dry nitrogen was passed across the surface of the solution. When the blue colour of the solution of lithium in liquid ammonia had been discharged by the addition of a further quantity of hydrated ferric nitrate (0.02 gm), 2-bromo-3-diethylaminoprop-1-ene (30 gms) was added and the grey mixture stirred at -40°C for four hours under a slight positive pressure of nitrogen.

A solution of perinaphthen-1-one (18.2 gms) in anhydrous ether (80 mls) was then added dropwise over a period of thirty minutes and the mixture stirred for a further eight hours, the temperature being maintained at -40°. After this time, powdered ammonium chloride (10 gms) was added and the ammonia was allowed to evaporate off by standing the reaction flask overnight in a bath of ethanol.

The residue was then treated with an excess of 2 N sulphuric acid (250 mls). The non-basic material was removed from the acid mixture by extraction into ether (2 x 200 mls). The ether extracts were washed successively with water (100 mls), 5% sodium hydroxide solution (150 mls) and water (150 mls) and dried ($MgSO_4$).

The aqueous acid phase was filtered and made alkaline with

concentrated ammonia solution. This alkaline mixture was extracted with ether (2 x 200 mls) and the aqueous phase was discarded. The ether extracts were washed with water (2 x 150 mls) until the washings were neutral, and dried (Na_2SO_4). Removal of the solvent left a brown solid which, after two sublimations at 130-150°C / 0.1 m.m yielded colourless prisms of 1-(3-diethylaminoprop-1-ynyl)-perinaphthen-1-ol (11.6 gms; 70% based on perinaphthenone used). After one recrystallisation from benzene, the m.pt. was 126-127°C.

Analysis: Found C 81.91 H 7.95 N 4.64

$C_{20}H_{25}ON$ requires C 81.90 H 7.90 N 4.77

The solvent was removed from the non-basic ether extract and the residual oil was dissolved in a mixture of light petroleum (30 mls) and benzene (5 mls), before chromatography on a column of alumina (15 x 3.2 cms). The column was developed and eluted with a mixture of light petroleum and benzene (1:1). Removal of the solvents from the yellow eluates (350 mls) and crystallisation of the residue from methanol, yielded perinaphthen-1-one (3 gms), m.pt. 79.5-81°C.

C.II.5. Attempted dehydration of 1-(3-diethylaminoprop-1-ynyl)-perinaphthen-1-ol: First experiment.

A mixture of the alcohol (1.1 gms), formic acid (S.G. 1.2; 5 mls) and 90% phosphoric acid (1.1 ml) was boiled gently under reflux for six hours; the cooled solution was then poured into water (30 mls).

Extraction with chloroform (2 x 50 mls) removed most of the red colour from the aqueous solution. After basification with concentrated ammonia solution, the aqueous solution was extracted with ether (2 x 50 mls). The ether extract was washed with water (3 x 50 mls) and dried (Na_2SO_4), and the solvent was removed leaving a black tar which resisted attempts to purify it by distillation or crystallisation.

The chloroform extract was washed with water (2 x 50 mls) and dried (Na_2SO_4); removal of the solvent left a dark red solid (730 mgms), with an indefinite crystalline form. After recrystallisation of a sample from methanol, the m.pt. was above 300°C.

Analysis: Found C 76.16 H 6.55 N 2.36%

The remainder was dissolved in a minimum of boiling methanol, the solution cooled and perchloric acid added dropwise. The precipitated red solid melted above 300°C.

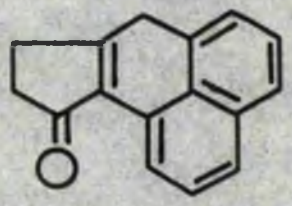
Analysis: Found C 66.16 H 5.72 N 2.45%

C.II.4. Attempted dehydration of 1-(3-diethylaminoprop-1-ynyl)-perinaphthan-1-ol: Second experiment.

A solution of the acetylenic alcohol (0.5 gm) in acetic anhydride (25 mls) was boiled under reflux for eighteen hours. The solution, originally pale yellow in colour, turned dark green. After cooling, it was poured into water (150 mls). All that could be isolated by ether extraction of this solution and working up in the

normal manner was an intractable black tar.

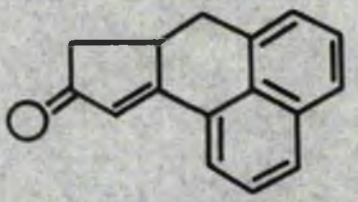
C.II.5. Attempted conversion of 1-(3-diethylaminoprop-1-ynyl)-perinaphthan-1-ol to 10-oxo-7,8,9,10-tetrahydrocyclopenta[a] perinaphthene (CLV).



(CLV)

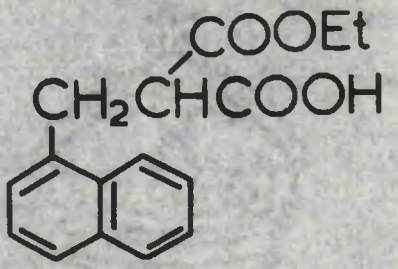
A mixture of the acetylenic alcohol (2.9 gms), formic acid (S.G. 1.2; 6 gms) and 90% phosphoric acid (1.8 gms) was boiled under gentle reflux for six hours. Mercuric acetate (0.5 gm) was then added and the boiling under reflux was continued for a further four hours. The tarry product was poured into water (100 mls) and basified with 2 N sodium hydroxide solution. This solution was extracted with chloroform (2 x 100 mls) and the chloroform extract was washed first with dilute acid (in order to remove unchanged basic material) until the acid washings were colourless, and then with water; it was then dried over sodium sulphate. Removal of the solvent by distillation left a black solid (470 mgms). Attempts to purify this material by crystallisation or sublimation were of no avail.

C.III. The Projected Synthesis of 9-Oxo-7,7a,8,9-Tetrahydrocyclopenta[a] perinaphthene (CLXXIII).



(CLXXIII)

C.III.1. Ethyl hydrogen α-naphthylmethyl malonate.



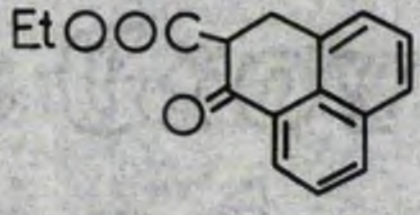
225.5 Mls of a solution of potassium hydroxide (140 gms) in ethanol (160 mls) was added to a stirred solution of diethyl α-naphthylmethyl malonate (104.8 gms), prepared by the method described by Fieser and Gates[88], in ethanol (1 litre) over a period of forty-five minutes. The solution was stirred for a further three hours and allowed to stand overnight at room temperature. One-half of the solvent was distilled off and the remainder of the solution was poured into an equal volume of water and acidified (HCl). The acid mixture was extracted with ether (2 x 1 litre portions) and the pale yellow ether extract was washed well with water (3 x 750 mls), followed by

two portions of saturated sodium bicarbonate solution (1 litre and 300 mls). The yellow colour was transferred to the bicarbonate layer which was washed once with ether (250 mls) before acidification (HCl). The acidified solution was extracted with ether (2 x 1 litre portions) and the combined ether extracts were washed with water (4 x 500 mls) and dried (Na_2SO_4). Evaporation of the solvent left 76.5 gms (80.5%) of a pale yellow oil which lost carbon dioxide on attempted distillation.

Neutralisation Equivalent: Found 276

Required 272

C.III.2. Ethyl 2-carboxy-3-oxo-1,2,3,4-tetrahydrophenanthren-1-one



Ethyl hydrogen α-naphthylmethyl malonate (15.5 gms) was added to anhydrous liquid hydrogen fluoride (100 mls) and the solution was allowed to stand at room temperature for 6½ hours. It was then poured on to crushed ice (200 gms) and the organic material was taken up in ether (250 mls). The ethereal solution was washed with water (2 x 200 mls), extracted with saturated sodium bicarbonate solution (5 x 100 mls) until the alkaline extract was colourless, washed again with water (200 mls) and dried (Na_2SO_4).

The bicarbonate extract was filtered and acidified (HCl). The precipitated yellow oil was taken into ether (150 mls) and the ethereal solution was washed with water (4 x 50 mls) and dried (Na_2SO_4). Evaporation of the solvent left a dark yellow oil (10.12 gms) with a neutralisation equivalent of 286. Ethyl hydrogen α-naphthylmethyl malonate requires a value of 272.

Removal of solvent from the ethereal solution which had been washed with bicarbonate left 5.4 gms (67.5%, based on the half ester used) of a pale yellow oil which was purified by distillation in a closed system at 190-200° / 0.5 m.m. The distillate was pale yellow in colour and gave a green colouration with alcoholic ferric chloride solution. It was insoluble in concentrated acid.

Analysis: Found C 79.84,79.12 H 7.0, 6.63%

$C_{16}H_{14}O_3$ requires C 75.58 H 5.53%

C.III.3. Attempted condensation of ethyl 2-carboxyperinaphthan-1-one with propargyl bromide.

A mixture of sodium ethoxide, from sodium (0.35 gm) and ethanol (30 mls), and ethyl 2-carboxyperinaphthan-1-one (3.8 gms) was boiled under reflux for thirty minutes. Propargyl bromide (2.065 gms; 1.31 mls) was then added to the boiling solution over thirty minutes and refluxing was continued for a further 2½ hours. After about one half of the ethanol had been distilled off, the solution was poured into water (150 mls) and the aqueous mixture was extracted with ether

(2 x 100 mls). The ethereal solution was washed with water (3 x 100 mls), dried (Na_2SO_4), and the solvent evaporated leaving a dark red oil (4.4 gms). On extraction from benzene solution with 2 N sodium hydroxide solution this gave only a very faint pink colour in the alkaline layer. The red oil was purified by two distillations in closed systems at 190°C / 0.5 m.m. The distillate was a pale yellow oil which gave a green colouration in ethanol solution with ferric chloride solution.

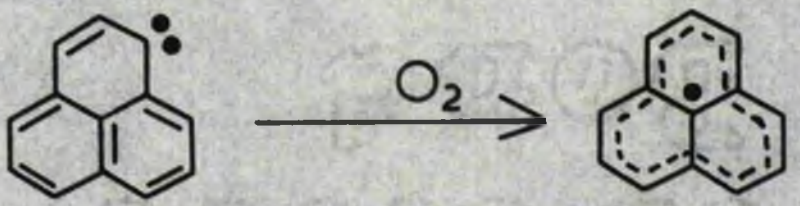
Analysis: Found C 79.20 H 6.95%

$C_{19}H_{16}O_5$ requires C 78.10 H 5.52%

C.IV. Preparations and Properties of Perinaphthyl.

(CXXXXIII)

C.IV.1. Perinaphthyl from the perinaphthenide anion.



(CLXXV) (CXXXXIII)

A solution of perinaphthene (850 mgms), prepared by the method described by Bockelheide and Larrabee[105], in ether (40 mls) was placed in a conventional hydrogenation flask of 100 ml capacity carrying a small reservoir in which was placed absolute ethanol (0.8 ml). Dry potassium methoxide (400 mgms) was added to the ethereal solution which was then connected to a conventional hydrogenation apparatus filled with oxygen. After the apparatus had been closed, the ethanol was allowed to flow into the mixture and the oxygen level quickly read. Shaking was started and the solution of perinaphthene which initially became red (formation of potassium perinaphthenide) rapidly turned blue as oxygen was absorbed and a considerable quantity of a green solid (perinaphthyl peroxide)

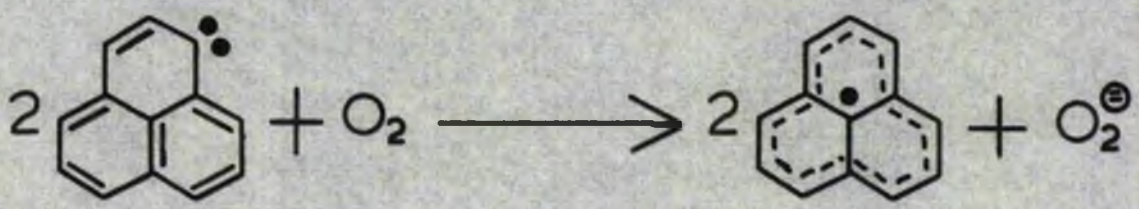
precipitated from the ether solution. When approximately 75 mls of oxygen had been taken up, the reaction was terminated by the addition of water after disconnecting the reaction flask from the oxygen reservoir. The total contents of the flask were transferred to a one-litre separating funnel using ether and water to wash out the contents. About 200 mls ether were added to the separating funnel with approximately 200 mls water. The dark green peroxide was filtered off and the ether layer was washed with water (2 x 200 mls), dried (K_2CO_3), and the filtered solution (ca 250 mls) chromatographed without delay on a column of alumina (15 x 3.2 cms). The radical travelled down the column rapidly and was obtained as a clear blue solution freed from yellow material which was formed on exposure of the radical to light and which travelled down the column much more slowly. It was not necessary to use further eluant; the bulk of the radical was collected in 250-300 mls solution. The clear blue eluates were collected as long as they showed no blue fluorescence.

The radical showed a broad absorption maximum at 610-615 mμ with a flat peak at 612-615 mμ. Plate IV shows the visible absorption spectrum of perinaphthyl, prepared by this method.

C.IV.2. Perinaphthyl from the perinaphthenide anion: The relationship between oxygen absorption and time.

A solution of perinaphthene (4.98 gms) in ether (240 mls) was placed in a conventional hydrogenating flask of 500 ml capacity carrying a small reservoir in which was placed absolute ethanol (4.8 mls). Dry potassium methoxide (2.4 gms) was added to the ethereal solution which was then connected to a conventional hydrogenation apparatus filled with oxygen. After the apparatus had been closed, the ethanol was allowed to flow into the mixture and the oxygen level quickly read. Shaking was started and the oxygen level was noted at ten second intervals for 8½ minutes and subsequently, at thirty second intervals. The plot of the volume of oxygen absorbed against time is shown on Plates I and II.

C.IV.3. Perinaphthyl from the perinaphthenide anion: The relationship between oxygen absorption and peroxide ion concentration.



(CLXXV) (CXXXIII)

This experiment was carried out a number of times for different volumes of oxygen absorbed, the oxygen absorption being varied between

five and sixty cos.at room temperature and pressure. A solution of perinaphthene (330 mgms) in ether (40 mls) was placed in a conventional hydrogenating flask of 100 ml capacity carrying a small reservoir in which was placed absolute ethanol (0.8 ml). Dry potassium methamide (400 mgms) was added to the ethereal solution which was then connected to a conventional hydrogenation apparatus filled with oxygen. After the apparatus had been closed, the ethanol was allowed to flow into the mixture and the oxygen level quickly read. Shaking was started and when a fixed volume of oxygen had been absorbed, the reaction was terminated by the addition of distilled water after disconnecting the reaction flask from the oxygen reservoir. The total contents of the flask were filtered in order to remove solid material and the aqueous layer separated. The organic layer was washed with a fresh portion of water and the aqueous layers combined. Determinations of peroxide content were carried out by titration against standard sodium thiosulphate. Plate III shows a plot of the peroxide ion concentration determined analytically against peroxide ion concentration calculated from the volume of oxygen absorbed. The results obtained from this series of experiments are tabulated below:-

Temp. °K	Press. m.m.	Vol. O_2 absorbed (ccs)	Vol. O_2 at N.T.P (ccs)	Vol. of .2009 N thiosulphate (ccs)	Wt. of O_2 $\ominus$ experimental (mgs)	Wt. of O_2 $\ominus$ calculated (mgs)
294	761.5	10.6	9.6	3.63	11.7	13.7
295	754	21.0	19.2	9.67	31.1	27.3
294	760	29.0	26.8	12.92	40.8	38.2
297	755	30.8	27.9	15.98	44.9	30.8
291	760	38	35.5	16.60	52.6	50.7
294	766	48.9	45.5	20.64	66.3	64.9
291	770	51.5	49.0	23.0	73.9	69.9
294	767	61.6	57.4	24.64	79.2	81.9

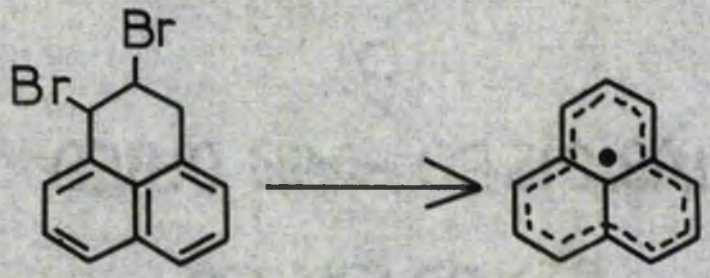
Wt. of perinaphthene (mgs) 350

C,IV,4. Perinaphthyl from perinaphthene by reaction with N-bromo-succinimide.

N-Bromosuccinimide (0.55 gm) was added to a solution of perinaphthene (0.50 gm) in carbon tetrachloride (25 mls). After shaking for five minutes at room temperature the solution turned brown and, on exposure to the atmosphere, it turned dark green with liberation of hydrogen bromide. This solution was passed down a column of alumina (15 x 3.2 cms) using ether as eluant and the blue radical was obtained in 250 mls of solution. A strong orange band, indicative of the presence of peropyrene, was retained at the top of the column.

The absorption spectrum of perinaphthyl prepared by this method was identical in the region 750-500mμ with that of perinaphthyl prepared from the perinaphthenide anion.

C.IV.3. The dehydrobromination of 2,3-dibromoperinaphthane.

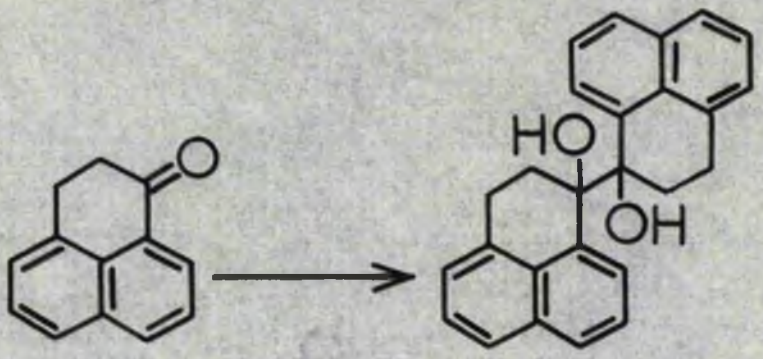


(CLXVI) (CXXXIII)

2,3-Dibromoperinaphthane was prepared in 61% yield by the method described by Bosselheide and Larrabee[105]. It was isolated as pale yellow, almost colourless, prisms, m.pt. 95-97°C (lit.,103-104°C). In accord with the findings of Bosselheide and Larrabee, the compound lost hydrogen bromide and bromine on standing and became dark brown in a short period of time.

2,3-Dibromoperinaphthane (0.30 gm) was shaken in pyridine (25 mls) at room temperature. After three minutes, the solution was poured into water (100 mls) and the aqueous mixture extracted with ether (2 x 25 mls). The ether extracts were washed with water (2 x 25 mls) and dried (K_2CO_3) prior to chromatography on a column of alumina (12 x 2.5 cms) using ether as eluting solvent. Perinaphthyl was obtained in 150 mls solution; it showed the characteristic absorption maximum at 615mμ.

C.IV.6. The Bimolecular Reduction of Perinaphthan-1-one.



(L) (CLXXVI)

Mercuric chloride (300 mgms) and aluminium turnings (5.75 gms) were added in rapid succession, in that order, to a solution of perinaphthan-1-one (18.2 gms) in a mixture of anhydrous ethanol (90 mls) and dry, thiophen-free benzene (60 mls). Within 5-10 minutes the mixture began to boil spontaneously and after the vigour of the reaction had begun to slacken, boiling under reflux was continued for a further two hours when practically all the aluminium had dissolved. The mixture was poured into water, to which ether was then added, and both the aqueous and organic phases filtered to remove a grey precipitate which had come out of solution.

The aqueous-ether-benzene mixture was shaken up and the organic layer collected, washed thoroughly with water to remove ethanol, dried (K_2CO_3) and the solvent was removed. A small quantity of benzene was added and the solution, after standing overnight, deposited the diol (CLXXVI) (130 mgms) as colourless cubic crystals.

The solid which had been filtered from the hydrolysis mixture was extracted with boiling amyl alcohol (4 x 75 mls) and the diol (870 mgms)

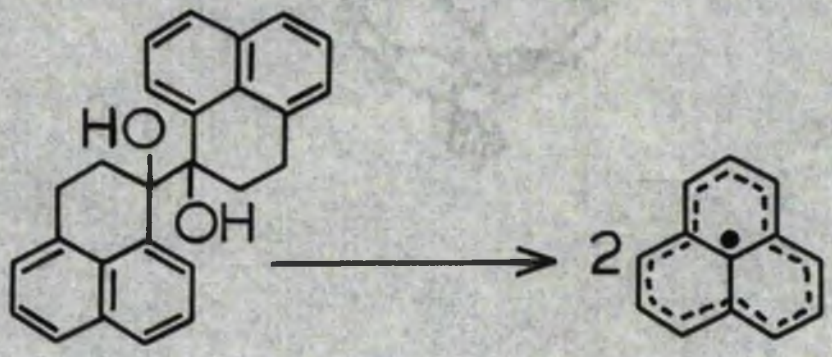
crystallised from the cooled extracts as colourless cubic crystals. A further quantity (200 mgms) was obtained on concentration of the mother liquors to low volume.

A sample recrystallised from amyl alcohol as colourless needles, which slowly turned yellow on exposure to light, m.pt. 253-255.5°C. The melting point depends on (a) rate of heating (b) when the sample was placed on the block and (c) on the glass cover slips. The melting point given is the mean of several recorded under similar conditions (a) slow heating and (b) placing on the block at 250°. The highest melting point recorded was 256-256.5°C.

Analysis: Found C 85.51 H 6.08%

$C_{26}H_{22}O_2$ requires C 85.21 H 6.15%

C.IV.7. Dehydration of 1-1'-Diperinaphthan-1-ol (CLXXVI)



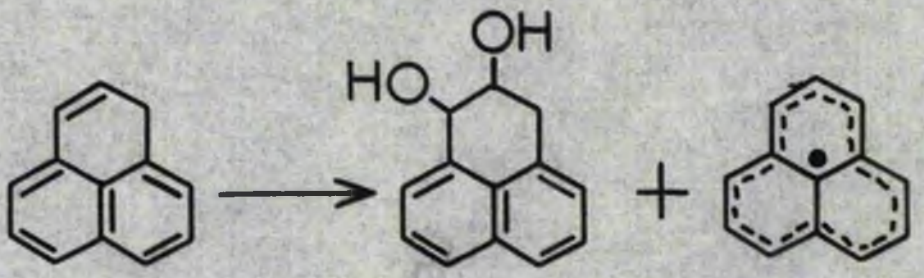
(CLXXVI) (CLXXVII)

The diol (800 mgms) was dissolved in boiling propionic acid (50 mls), the resulting solution becoming bright yellow. Concentrated hydrochloric acid (0.1 ml) was added to the hot solution which

immediately became greenish-blue (formation of the perinaphthyl radical). This colour faded in a few seconds and the now clear yellow solution possessed a strong fluorescence, characteristic of peropyrene. The solution was boiled under reflux for fifteen minutes, then concentrated to 5-10 mls. On cooling, peropyrene (72 mgms; 37%) crystallised as golden yellow leaflets, m.pt. above 350°C. The ultra-violet absorption maxima of peropyrene prepared by this method lay at 442,415,389,370,327 and 312 millimicrons.

The mother liquors from a similar run using the diol (100 mgms) in propionic acid (30 mls) to which concentrated hydrochloric acid (0.5 ml) was added, were poured into water, and the precipitated pale yellow solid collected in light petroleum. After working up in the usual fashion and removal of the solvent, the residual yellow oil on trituration with light petroleum gave a crude pale yellow crystalline solid (30 mgms). This, on recrystallisation from acetone-light petroleum, gave a pale yellow, almost colourless, solid (1.6 mgm) as plates. This is the compound (CLXXXVI) referred to in B,II,3 (b).

C.IV.8. Perinaphthyl from perinaphthene by reaction with osmium tetroxide.



(XLVIII) (CLXXVII) (CLXXIII)

The benzene used in this reaction was purified as follows. AnalaR benzene was boiled under reflux for three hours over anhydrous aluminium chloride and the bulk was recovered by distillation. The distillate was washed successively with water, saturated sodium bicarbonate solution (several times) and water and dried over anhydrous sodium sulphate. It was then fractionally distilled from sodium and, finally, stored over sodium wire.

A solution of freshly prepared perinaphthene (2.00 gms) in pure dry benzene (25 mls) was added to a solution of osmium tetroxide (3.91 gms) in benzene (25 mls) whereupon the mixture turned dark brown. AnalaR pyridine (2.00 mls) was at once added to the mixture which warmed up considerably while a black complex began at once to separate from solution. The mixture was allowed to stand at room temperature for ninety minutes, then an equal volume (50 mls) of cyclohexane was added and the mixture filtered. The residual greyish-black solid was washed with cyclohexane until the washings were colourless (approximately 150 mls) and dried at room temperature.

The deep-green filtrate obtained after removal of the solid was washed successively with 4 N sulphuric acid and water and dried (K_2CO_3). The solution was then chromatographed on a column of alumina (10 x 3.2 cm). A clear blue band passed down the column on continued development with cyclohexane and the perinaphthyl radical was found to be present. Thus, addition of a benzene solution of iodine gave the black perinaphthenylium iodide. Continued development of the column with ether brought through peropyrene, which, after recrystallisation from nitrobenzene, formed orange yellow plates, m.pt. above 350°. The ultra-violet absorption spectrum measured in benzene solution was identical with that of peropyrene prepared from perinaphthyl peroxide (Plate VI).

The greyish-black complex (8.0 gm; 90% based on cerium tetroxide used) was shaken up for ninety minutes in the presence of methylene chloride (200 mls) and a solution of potassium hydroxide (10 gms) and mannitol (10 gms) in water (150 mls). The aqueous phase rapidly became deep wine-red in colour but not all of the solid disappeared; part remained suspended as a greyish-black solid which failed to go into solution. The two phases were filtered to remove undissolved solid (800 mgms) as a black amorphous powder, and the two layers were then separated.

The aqueous alkaline layer, deep wine-red in colour, was washed twice with methylene chloride and the washes combined with those obtained as described below.

The methylene chloride phase was again shaken up with a solution of potassium hydroxide (10 gms) and mannitol (10 gms) in water (150 mls) for two hours. The aqueous-alkaline layer again became coloured wine-red but not intensely so. After filtration to remove traces of suspended solid, the methylene chloride layer was retained and the aqueous alkaline layer washed with two portions of methylene chloride which were combined with the original methylene chloride solution.

The combined methylene chloride solutions and washes were washed successively with 5% potassium hydroxide solution and water and dried (K_2CO_3). The methylene chloride solution thus obtained retained a brown colour. After concentration to approximately 150 mls the solution was subjected to a preliminary chromatographic analysis on a column of alumina (6 x 2.7 cm). Development was carried out first with pure methylene chloride. This brought through a deep yellow band as orange-yellow eluates; a brown band was retained at the top of the column. Development was continued using methanol which brought through the brown band containing the desired diol. The two sets of eluates were worked up separately.

The methanol eluates, approximately 500 mls in volume and brown in colour, were evaporated to dryness. A crystalline solid was left and was redissolved in methylene chloride. This solution was chromatographed carefully (to remove traces of the orange-yellow substance) on a column of alumina (10 x 3.2 cm) and elution first carried out with methylene chloride until the orange-yellow substance

had been completely removed and the methylene chloride eluates were colourless. The brown band at the top of the column was now washed through completely with methanol (approximately 400 mls) and the methanol eluates concentrated to approximately 100 mls. Water (200 mls) was then added and the boiling solution charcoal screened. The colourless filtrate was evaporated to low volume when perinaphthan-1,2-diol (460 mgms; 15%) crystallised as colourless needles, m.pt. 142-144°. It was necessary to extract the charcoal at least twice to retain all of the diol. The melting point was not raised after sublimation at 120-130°C / 0.1 m.m.

Analysis: Found C 78.88 H 6.07%

$C_{13}H_{12}O_2$ requires C 78.00 H 6.04%

C.IV.9. The Dissociation and Disproportionation of Perinaphthyl.

The solvent used for chromatography and for the preparation of solutions for spectrophotometric examination was ether, carefully purified as follows.

Approximately 3.5 litres of anaesthetic ether was shaken intermittently with 500 mls of a 10% solution of sodium metabisulphite for forty-five minutes. The bisulphite layer was removed and discarded and the ether layer washed free of bisulphite with water (two or three times) and then shaken with 500 ml of a 1% potassium permanganate solution containing potassium hydroxide (20 gms) for

ten to fifteen minutes. The ether was then washed free of permanganate and allowed to stand for twelve hours over 10% sodium bisulphite solution (500 ml). The ether was then washed thoroughly with water, dried over calcium chloride for nine hours and, after removal of the calcium chloride by filtration, was allowed to stand overnight over sodium wire. It was then distilled through a Vigreux column (seven steps) and stored in a dark bottle. Directly before use the ether was treated with lithium aluminium hydride (1 gm / 2 litres), allowed to stand for several hours, and again distilled through a Vigreux column.

The perinaphthyl radical was prepared as already described (C,IV,1) using perinaphthene (280 mgms), potassium methoxide (400 mgms), absolute ethanol (0.8 ml) and dry ether (40 mls). The radical was thus obtained in approximately 150-180 mls ether prior to chromatography.

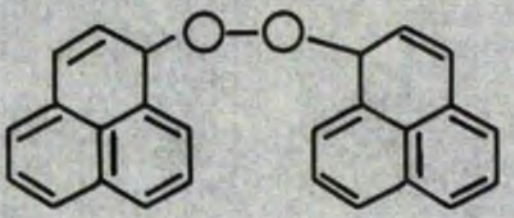
The ether solution was chromatographed on a large column of alumina (17 x 4.2 cm), using purified ether to prepare the column and, if necessary, to develop it. When the blue eluates began to issue from the column, the time was noted and sufficient of the eluates collected to prepare 500 mls solution of suitable concentration for spectrophotometric analysis. It was found that this was best done by pumping the eluates into approximately 400 mls purified ether contained in a 500 ml standard flask until the depth of colour was estimated visually as corresponding to a suitable concentration.

The time at which the filtrates issued from the column was taken as zero time i.e. at this time the concentration of the solution was assumed to be 100% with respect to the radical and 0% with respect to the dimer. Spectrophotometric determinations were then made as soon as possible after this time. The time which elapsed between the point at which the eluates first began to issue from the column and the point at which the first spectrophotometric determination was made was found to be not greater than ten minutes.

Readings of the optical density were made at suitable time intervals (2.5, 5, 10 minute periods etc.). A fresh sample of solution and solvent was used for each reading since it was noted that exposure of the radical solution to light of the wavelength used (615mμ) caused a rapid decrease in the absorption. Plate V shows the decrease in optical density with time.

The determinations were carried out at a temperature of 20.5 - 21.5°C.

C.V. Perinaphthyl peroxide (CLXXXVII)



(CLXXXVII)

C.V.i. Perinaphthyl peroxide: Preparation.

Absolute ethanol (1.6 ml) was added to a suspension of potassium methoxide (800 mgms) in a solution of perinaphthene (1.66 gm) in absolute ether (80 ml) contained in a 250 ml hydrogenation flask connected to a graduated oxygen reservoir. The mixture was shaken until just over two moles of oxygen had been absorbed (245 mls at N.T.P.; calculated for complete conversion to the peroxide, 224 mls at N.T.P.). The green peroxide was filtered through a sintered glass funnel, well washed with ether (400 mls), then with water until the issuing filtrates, originally orange-brown, were only light yellow and reacted neutral to litmus.

The greenish-yellow granular solid residue was further washed with ether until the filtrates were only light yellowish green and was dried in vacuo over phosphorus pentoxide prior to analysis. It showed no definite melting point.

Analysis: Found C 85.67 H 4.91%

$C_{20}H_{12}O_2$ requires C 86.18 H 5.00%

The alkaline filtrates were washed once with ether and filtered free of traces of solid before acidification. The small quantity of yellow solid thus precipitated was collected in ether and, after washing free of acid, was worked up in the usual fashion. A smear of an oily solid remained after removal of the solvent but the small quantity prevented further investigation and it was therefore discarded.

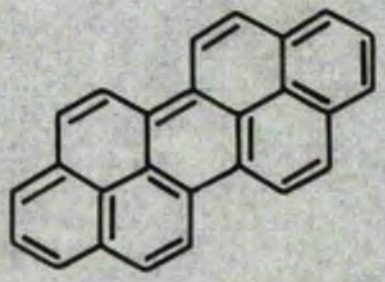
The green ether washings which were obtained prior to the washing of the green solid with water were washed neutral with water and dried (Na_2SO_4) before concentration. On reaching low volume, the solution lost its deep green colour completely and became yellow with a typical fluorescence similar to that obtained when the perinaphthyl radical is heated or allowed to stand for several days. The solid obtained on complete removal of the solvent was orange-red and tacky. It was sublimed at 100-150°C / 0.5 m.m. giving a yellow crystalline solid (430 mgms) which, after one crystallisation from methanol, melted at 148-151° and did not depress the melting point of an authentic sample of perinaphthenone. It dissolved in concentrated hydrochloric acid giving an orange solution.

<u>G.V.2. Perinaphthyl peroxide : Decomposition.</u>

A sample of the dry solid, obtained as described above, was gradually heated at 0.5 to 1 m.m. A yellow sublimate formed at 120-150°C in small amount and proved to be perinaphthenone (m.pt. and

mixed m.pt.). A considerably larger deposit, dull brownish yellow in colour, collected at 280-300°C. This was pure pyrene; it gave a clear blue solution with concentrated sulphuric acid.

C.VI. Preparations of Perocyrene (LXVI).



(LXVI)

C.VI.1. Perocyrene from perinaphthene.

Potassium methoxide (4 gms) was added to a solution of perinaphthene (8.5 gms; 0.05 mol) in ether (400 mls) contained in a hydrogenation flask from which air was swept out with oxygen. Dry ethanol (8 mls) was added and the oxygenation started immediately; shaking was continued until 1120 mls oxygen had been absorbed (two hours), the colour of the solution changing through blue to dark green. The solution was then filtered and the dark green peroxide cake washed well with ether, then with hot water, and dried in vacuo over phosphorus pentoxide. The dry peroxide (7.85 gms) was then Soxhlet extracted using benzene (2 x 1 litre portions) for twenty-nine hours. The benzene extracts were concentrated to a volume of 50 mls and chromatographed on a column of alumina (10 cm x 4 cm), using benzene as eluting solvent; the eluate (500 mls) was concentrated to a volume of 50 mls and rechromatographed on a column of alumina (10 cm x 4 cm). The eluates on concentration to 50 mls gave perocyrene (1.5 gms; 18%)

which, after recrystallisation from nitrobenzene, was obtained as orange-yellow plates melting above 360°C. The ultra-violet absorption spectrum of peropyrene prepared by this method is shown on Plate VI.

C.VI.2. Peropyrene from perinaphthenone.

This preparation is based on the method described by Clar[190]. A mixture of perinaphthenone (2.5 gms), zinc dust (2.5 gms), sodium chloride (2.5 gms) and fused, granular zinc chloride (12.5 gms) was heated in an open flask at 250°C for three minutes. After cooling, the mass was washed with concentrated hydrochloric acid (200 mls) and then boiled with 2 N hydrochloric acid (200 mls) for fifteen minutes. The acid solutions were discarded and the dried residue was placed in a Soxhlet thimble above a boiling solution of benzene (600 mls) and the extraction was continued for six hours. The benzene extract was concentrated to a volume of 100 mls and chromatographed on a column of alumina (10 x 4 cm) using benzene as the eluting solvent. On concentration to low volume, the eluate (750 mls), which showed the yellow colour and greenish-blue fluorescence of peropyrene, yielded the hydrocarbon (1.1 gm; 30%) which, after one recrystallisation from xylene, formed golden yellow leaflets melting above 350°C.

C.VII. The Perinaphthenylium Cation (CXVII).

(CXVII)

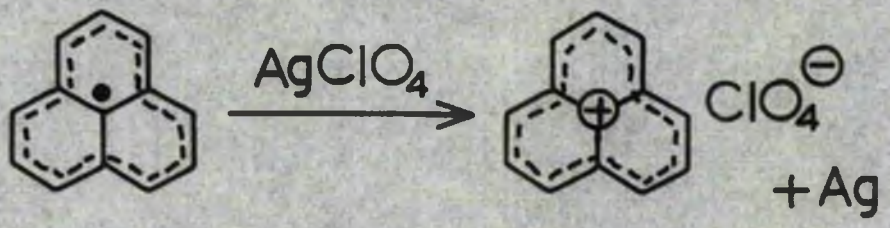
C.VII.i. Perinaphthenylium Iodide (CXXXVI)

An ethereal solution of perinaphthyl, prepared as described above (CIV,i) by the action of potassium methoxide on perinaphthene (300 mgms) in 1% ethanolic ether, was treated dropwise with a solution of iodine in benzene (approximately 2 gms iodine per 150 mls benzene) until the blue colour of the radical had almost disappeared. A black solid came out of solution and was removed at once by filtration. There was thus obtained after washing with small amounts of benzene, acetone and light petroleum, perinaphthenylium iodide (190 mgms; 13% based on perinaphthene used). This showed no definite melting point, was insoluble in ether, light petroleum, benzene and chloroform, coloured acetone faintly, but dissolved readily in polar solvents, especially in pyridine, morpholine, piperidine and nitrobenzene, less so in nitromethane and acetonitrile giving bluish-green to green solutions. These solutions become yellow on standing, this process being accelerated by boiling.

Analysis: Found C 54.41 H 3.83 I 42.30%

$C_{13}H_9I$ requires C 53.44 H 3.11 I 43.45%

C.VII.2. Perinaphthenylium perchlorate from perinaphthyl.



(CCCXXXIII) (CCCXVII)

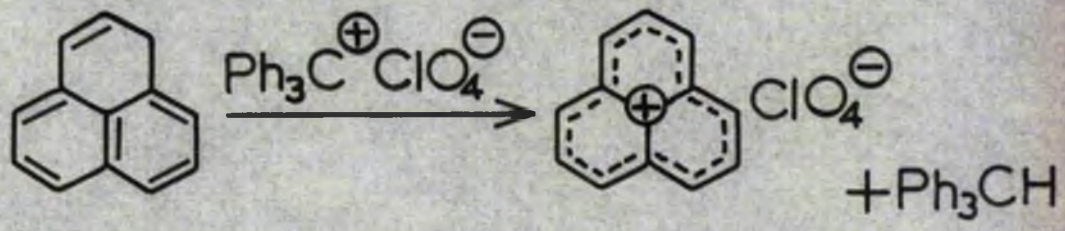
An ethereal solution of the perinaphthyl radical, obtained as described above by the action of potassium methoxide on perinaphthene (330 mgms) in 2% ethanolic ether, was treated with dry silver perchlorate until the blue colour of the radical was discharged. The precipitated black solid was filtered off and stored in vacuo. The combined products from six such runs were washed with toluene (250 mls), benzene (250 mls), and ether (50 mls) and then dried in vacuo over phosphorus pentoxide. The dry solid was warmed in nitromethane (50 mls) at 80° for fifteen minutes and the resulting mixture was filtered through a sintered glass funnel in order to remove metallic silver before dilution of the filtrate with ether (300 mls). The black precipitate which formed was filtered off, washed with a little benzene and light petroleum and dried in vacuo over phosphorus pentoxide. The yield was 138 mgms (10% based on perinaphthene used).

Analysis: Found (i) C 77.95 H 4.22 Cl 4.14%

(ii) C 71.90 H 5.80 Cl 7.88%

$C_{13}H_9ClO_4$ requires C 59.15 H 3.44 Cl 13.45%

C.VII.3. Perinaphthenylium perchlorate from perinaphthene.



(XLVII) (CXXXVII)

A solution of triphenylmethyl perchlorate (686 mgms) in glacial acetic acid (90 mls) was added to a solution of perinaphthene (370 mgms) in glacial acetic acid (10 mls). After about five minutes at room temperature, the yellow crystalline precipitate was filtered off and washed successively with dry ether and light petroleum with due care to avoid exposure to the atmosphere. After drying in vacuo for five hours, the perchlorate (367.4 mgms; 61%) was decomposed with water (100 mls); the mixture was filtered through a sintered glass funnel in order to remove organic material and the solid was well washed with water. The perchlorate (ClO_4) content of the salt was estimated by titration of the aqueous solution against standard alkali using bromothymol blue as indicator.

Found ClO_4 37.2%

$C_{19}H_{15}ClO_4$ requires ClO_4 37.0%

A second experiment carried out exactly as above, yielded perinaphthenylium perchlorate (337.7 mgms). Found ClO_4 36.2%.

A third experiment was carried out under the conditions described above using solutions of triphenylmethyl perchlorate (345 mgms) in acetic acid (35 mls) and perinaphthene (180 mgms) in acetic acid (5 mls).

The yield of perinaphthenylium perchlorate was 165.8 mgms.

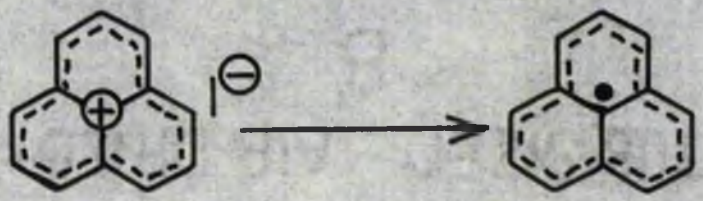
Found ClO_4 37.0%.

The organic material from the first and second experiments was combined and dissolved in benzene (150 mls). This solution was extracted with concentrated hydrochloric acid (4 x 150 mls) and the combined acid extracts were filtered and diluted with water (1½ litres). The resulting emulsion was extracted with benzene (2 x 500 mls) and the benzene solution was washed with water (500 mls), saturated sodium bicarbonate solution (2 x 200 mls) and water (500 mls). It was dried (Na_2SO_4) before removal of the solvent by distillation. Sublimation of the residue at 135°C / 0.1 m.m., followed by crystallisation of the sublimate from a mixture of benzene and petroleum ether yielded perinaphthenone (150 mgms; 59% based on the weight of perinaphthenylium perchlorate), m.pt. and mixed m.pt. with an authentic sample, 154-156°C.

The benzene solution which had been extracted with concentrated hydrochloric acid was washed with water, saturated sodium bicarbonate solution and water and dried (Na_2SO_4). Solvent was removed, the residue was dissolved in light petroleum (20 mls) and the resulting solution was passed through a column of alumina (12 x 3.2 cm) using light petroleum (200 mls) as eluting solvent. Removal of solvent from the eluate left perinaphthene (90 mgms) which was dissolved in ethanol (5 mls). A solution of trinitrobenzene (110 mgms) in ethanol (25 mls) was added, the solution boiled and crystallisation allowed to proceed. The yield of the trinitrobenzene complex of perinaphthene

was 150 mgms as orange needles, m.pt. 151-153° with decomposition (lit[105] 158°). After one further recrystallisation from ethanol, the melting point was not raised.

C.VII.4. Perinaphthyl from perinaphthenylium iodide.

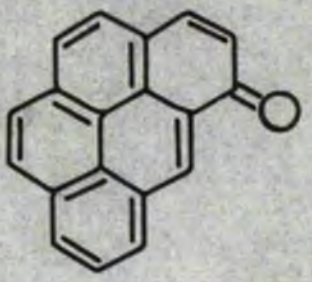


(CXXXVII) (CXXXIII)

Powdered perinaphthenylium iodide (100 mgms) was treated with dry pyridine at room temperature, whereupon the solvent became bluish green in colour. After shaking the mixture for four minutes, the solid dissolved to give a deep green solution. The solution was diluted with water (300 mls) and acidified (4N HCl) before being extracted with ether (300 mls). The blue ether extract was washed free of acid, dried (K_2CO_3) and the filtered solution chromatographed on a column of alumina (16 x 3.2 cm).

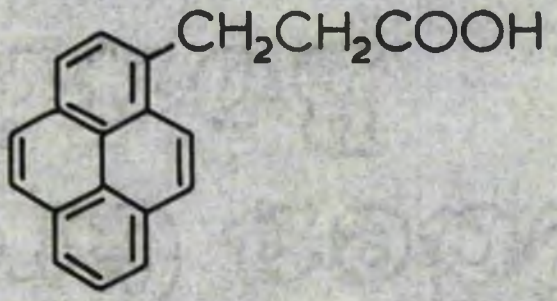
The clear blue eluates were examined spectroscopically (750 - 200 mμ) and the spectrum in the region 750-460 mμ was identical with that of perinaphthyl prepared from the perinaphthenide anion, showing a broad absorption maximum at 610-615 mμ with a flat peak at 612-615 mμ

C.VIII. The Synthesis of Naphtho[3,4,4a,5-g,h,i]-perinaphthenone (CXCV).



(CXCV)

C.VIII.1. β-3-Pyrenylpropionic acid.



This acid was prepared by the method described by Bachmann and Carmack[191].

C.VIII.2. Cyclisation of β-3-pyrenylpropionic acid using polyphosphoric acid[149].

β-3-Pyrenylpropionic acid (1 gm) was added to a solution of phosphorus pentoxide (45 gms) in 90% phosphoric acid (25 mls) and the mixture heated at 100°C for forty five minutes with frequent swirling. After cooling, the reaction mixture was poured into iced water (700 mls) and this solution was extracted with ether and chloroform. The organic

layer was washed with water (2 x 250 mls) and unchanged acid extracted with 10% potassium hydroxide solution (2 x 300 mls).

The alkaline extract was acidified and the precipitate dissolved in ether and worked up in the usual way. Removal of the solvent left pure β-3-pyrenylpropionic acid (0.880 gm), m.p.175-176°.

The ether / chloroform layer was concentrated to a volume of 3 mls and crystallisation allowed to proceed. The solid which was obtained formed dark red prisms (14 mgms), m.pt. 216 -218.5° and dissolved in concentrated hydrochloric acid giving a green solution. This compound was a perinaphthenone derivative as evidenced by the low carbonyl absorption frequency in the infra-red (1630 cm^{-1}), characteristic of the perinaphthenones (A,II,6).

C,VIII,3. Cyclisation of β-3-pyrenylpropionic acid chloride using stannic chloride.

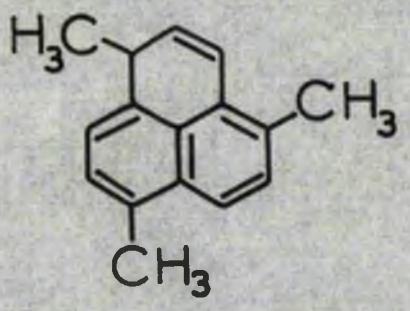
β-3-Pyrenylpropionic acid chloride was prepared by adding phosphorus pentachloride (0.84 gm) to a solution of the acid (1 gm) in benzene (10 mls). The solution was boiled under reflux for ten minutes, then cooled to room temperature and stannic chloride (0.64 ml) added. After thirty minutes at room temperature the mixture was poured into concentrated hydrochloric acid.(30 mls). There was considerable tar formation and the tar was dissolved in benzene. The acid layer was diluted with four times its volume of water and this

solution was extracted with benzene. The combined benzene extracts were washed with water (2 x 200 mls), followed by 10% potassium hydroxide solution (100 mls). Unchanged β-3-pyrenylpropionic acid (150 mgms), m.pt. 174 - 177°C was recovered from the alkaline extract.

The benzene solution was extracted with concentrated hydrochloric acid (4 x 50 mls) and washed with water (4 x 100 mls) and dried (Na_2SO_4). Evaporation of the solvent left a brown solid (300 mgms) from which no useful product could be isolated.

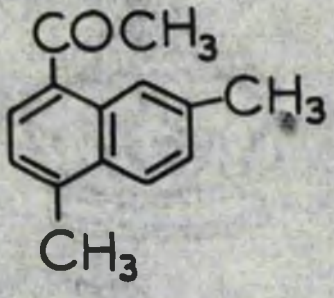
The green acid extract was diluted fourfold with water and the resulting mixture was extracted with benzene (2 x 200 mls). The benzene solution was washed with water (2 x 100 mls), saturated sodium bicarbonate solution (150 mls) and water (150 mls) and dried (Na_2SO_4). Removal of the solvent left a trace of a dark red solid which was too small in quantity to permit further purification.

C,IX. The Synthesis of 1,4,7-Trimethylperinaphthene (CCIV).



(CCIV)

C,IX,1. 4-Acetyl-1,6-dimethylnaphthalene (CCVI)



(CCVI)

A solution of acetyl chloride (66 gms) in 1,2-dichloroethane (150 mls) was added to a suspension of powdered, anhydrous aluminium chloride (115 gms) in 1,2-dichloroethane (335 mls) in a three-litre flask fitted with a mercury sealed stirrer, a dropping funnel and a reflux condenser. When solution was complete 1,6-dimethylnaphthalene (106 gms) in dichloroethane (600 mls) was added and the solution was stirred at room temperature for thirty minutes before being allowed to stand overnight at room temperature. The mixture was then boiled under reflux for ninety minutes and, after cooling, was poured into two litres of dilute hydrochloric acid. The dichloroethane layer was washed with water, saturated sodium bicarbonate solution and

water and dried (Na_2SO_4). Removal of solvent and distillation of the dark green residue gave 118 gms (86%) of ketone b.p. 135-140°C / 1 m.m. After further distillation (b.p. 118°C / 0.6 m.m.) followed by crystallisation from light petroleum, a sample of the ketone formed colourless plates, m.pt. 42-42.5°C. Feist[192] gives the melting point of the monoacetyl compound obtained from 1,6-dimethylnaphthalene with one or two mols acetyl chloride and one or two mols aluminium chloride in carbon disulphide or nitrobenzene as 45°C.

Analysis: Found C 84.37 H 7.08%

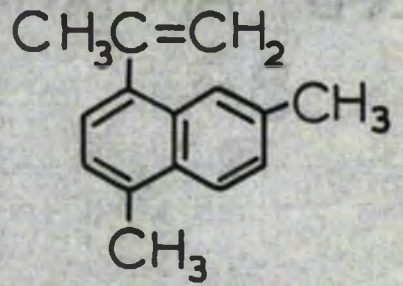
$C_{14}H_{14}O$ requires C 84.81 H 7.12%

The 2,4-dinitrophenylhydrazone was prepared in ethanol and after two recrystallisations from glacial acetic acid, formed red needles, m.pt. 250.5 - 252.5°C with slight decomposition.

Analysis: Found C 62.65 H 4.58 N 14.90%

$C_{20}H_{18}O_4N_4$ requires C 63.48 H 4.80 N 14.81%

C,IX,2. 1,6-Dimethyl-4-isopropenylnaphthalene.



A solution of 4-acetyl-1,6-dimethylnaphthalene (5.9 gms) in ether (25 mls) was added to the Grignard solution prepared from methyl iodide (2.9 mls) and magnesium turnings (0.87 gms) in ether (30 mls). After

addition of the ketone, the mixture was boiled under reflux for thirty minutes and then poured into ice-cold saturated ammonium chloride solution (150 mls). The ether layer was separated, washed with water (3 x 50 mls) and dried (Na_2SO_4). Removal of solvent by distillation left a pale yellow oil to which was added a solution of picric acid (7.2 gms) in ethanol (105 mls). The solution was boiled under reflux for 2½ hours and, after cooling, the picrate of 1,6-dimethyl-4-isopropenylnaphthalene (7.1 gms) was filtered off. After four crystallisations from ethanol, a sample formed orange needles, m.pt. 117-118°C (lit.[177] 118-119°C).

Analysis: Found C 50.27 H 4.34 N 9.90%

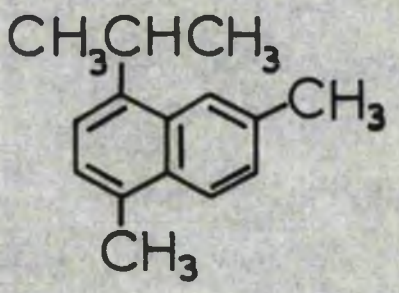
$C_{21}H_{19}O_7N_3$ requires C 50.29 H 4.50 N 9.88%

A suspension of the picrate (6.40 gms) in ether (150 mls) was washed several times with N ammonium hydroxide solution until the washings were colourless. The ethereal solution was washed with water (2 x 100 mls), dried (Na_2SO_4) and the solvent evaporated. Distillation of the residual oil yielded 1,6-dimethyl-4-isopropenylnaphthalene (2.25 gms) as a colourless mobile liquid, b.pt. 90°C / 0.6 m.m. (lit.[177] 134°C / 14 m.m.)

Analysis: Found C 91.94 H 8.31%

$C_{15}H_{16}$ requires C 91.78 H 8.22%

C,IX,3. 1,6-Dimethyl-4-isopropylnaphthalene (cadalene)



1,6-Dimethyl-4-isopropenylnaphthalene (1.29 gms) was hydrogenated in ethanol (50 mls) using 20% palladium on charcoal (200 mgms) as catalyst. The theoretical volume of hydrogen (150 mls) was absorbed during the first ten minutes, no further absorption taking place after a further ninety minutes shaking. Evaporation of solvent from the filtered solution and distillation of the residue yielded cadalene (0.94 gms) as a colourless mobile liquid, b.pt. 107°C / 1.5 m.m. (lit.[177] 153-154°C / 15 m.m.).

Analysis: Found C 90.97 H 9.00%

$C_{15}H_{18}$ requires C 90.85 H 9.15%

The picrate was prepared from the hydrocarbon (450 mgms) and picric acid (520 mgms) in benzene (5 mls). After two crystallisations from ethanol, the compound formed orange needles, m.pt. 113-116°C. (lit. 114-115°C[177][176][180] and 113-116°C[181]).

Analysis: Found C 50.16 H 3.14 N 9.50%

$C_{21}H_{21}O_7N_3$ requires C 50.01 H 4.95 N 9.83%

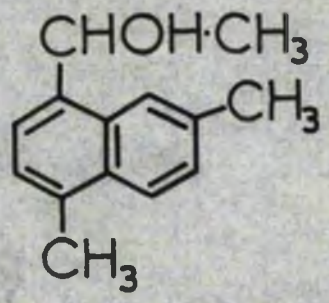
The trinitrobenzene complex was prepared from the hydrocarbon (400 mgms) and trinitrobenzene (450 mgms) in ethanol (15 mls). Three

recrystallisations of the product from ethanol yielded yellow needles m.pt. 109.5-110°C (lit. 111.5-115°C(181) and 112-115°C(195)).

Analysis: Found C 61.24 H 5.08 N 9.91%

$C_{21}H_{21}O_6N_3$ requires C 61.30 H 5.15 N 10.22%

C.III.4. Methyl-1,6-dimethylnaphthyl-4 carbinol.



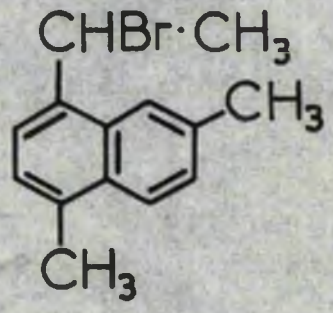
A solution of 4-acetyl-1,6-dimethylnaphthalene (76 gms) in ether (500 mls) was added to a suspension of lithium aluminium hydride (5.6 gms) in ether (1 litre) in a three litre flask fitted with a mercury sealed stirrer, a dropping funnel and a reflux condenser, at such a rate that the ether boiled gently. When addition of the ketone was complete, external heat was applied and the solution was boiled under reflux for a further hour when, after cooling, it was poured into 2 N sulphuric acid (1½ litres). The ether layer was separated, washed with water (2 x 1 litre portions), and dried (Na_2SO_4); evaporation of the solvent from the filtered solution left a pale yellow oil which solidified on standing overnight. The solid was dissolved in boiling light petroleum (700 mls) and crystallisation allowed to proceed. The product (69 gms; 90%) was obtained as colourless needles m.pt. 68.5-

69°C. The melting point was not raised by further crystallisation from light petroleum.

Analysis: Found C 84.16 H 8.04%

$C_{16}H_{16}O$ requires C 85.96 H 8.05%

C.IX.5. 4-(1-Bromoethyl)-1,6-dimethylnaphthalene (CCVII)



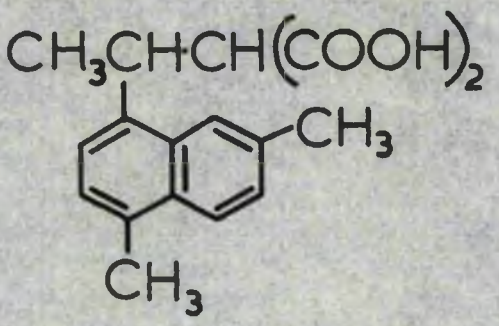
(CCVII)

Phosphorus tribromide (14 mls) was added to a cooled solution of the above alcohol (70 gms) in ether (500 mls) and the mixture was allowed to stand at room temperature for thirty minutes before being poured into water (1 litre). The ether layer was washed with water (2 x 500 mls), saturated sodium bicarbonate solution (500 mls) and water (500 mls) and dried (Na_2SO_4). Evaporation of solvent from the filtered solution and recrystallisation of the crystalline residue from a mixture of acetone and light petroleum (1:1) yielded the bromide (CCVII) (86 gms; 94%) as colourless, densely packed prisms, m.pt. 94-95°C.

Analysis: Found C 65.96 H 5.59 Br 30.30%

$C_{14}H_{15}Br$ requires C 65.89 H 5.75 Br 30.57%

C,IX,6. 2-(1,6-Dimethylnaphthyl-4)-1,1-dicarboxycyclopropane.



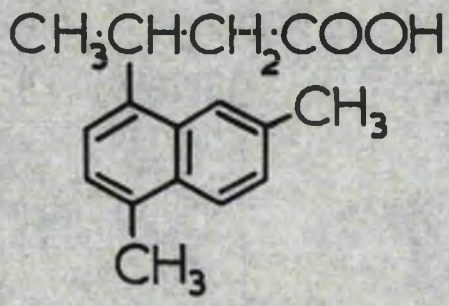
(CCVIII)

A solution of the above bromide (86 gms) in benzene (400 mls) was added to a cooled solution of sodio-malonic ester prepared from sodium (22 gms) and malonic ester (155 mls) in ethanol (750 mls). The mixture was allowed to stand at 0°C for two days and then boiled under reflux for two hours. The solvent was distilled off and the residue was boiled under reflux with 40% potassium hydroxide solution (1300 mls) for four hours. After cooling and dilution with an equal volume of water, the alkaline solution was washed with ether (2 x 750 mls), filtered and acidified (HCl). The precipitated acid (87 gms; 92%) was dried in vacuo over phosphorus pentoxide. A sample, recrystallised from water, formed colourless needles, m.pt. 137-139°C. Despite the extreme precautions taken during drying, a satisfactory carbon analysis could not be obtained.

Analysis: Found C 70.44 H 6.43%

$C_{17}H_{18}O_4$ requires C 71.31 H 6.34%

C.IX.7. β-(1,6-Dimethylnaphthyl-4)-butyric acid (CCIX).



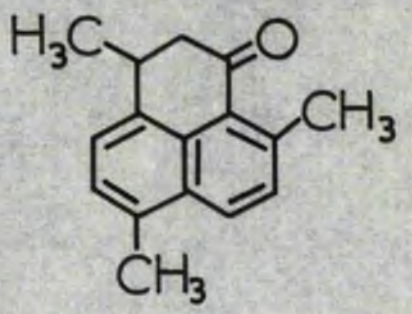
(CCIX)

The substituted malonic acid (CCVIII) (60 gms) was heated at 190-200°C until the evolution of carbon dioxide had ceased. The reaction was complete in thirty minutes and after a further five minutes the melt was allowed to cool while the flask was rotated to give a loose cake which was crystallised from a mixture of acetone and light petroleum (1:1) giving a first crop (40 gms) of colourless, densely packed prisms, m.pt. 121-122°C. The second crop (9 gms) after two further crystallisations from a mixture of acetone and light petroleum afforded 6 gms, m.pt. 121-122°C, making the total yield of pure β-(1,6-dimethylnaphthyl-4)-butyric acid 46 gms (90%).

Analysis: Found C 79.36 H 7.37%

$C_{16}H_{18}O_2$ requires C 79.30 H 7.49%

C.IX.6. 3,6,9-Trimethylperinaphthan-1-one (CCK)



(CCK)

β-(1,6-Dimethylnaphthyl-4)-butyric acid (74 gms) was added to anhydrous liquid hydrogen fluoride (300 mls) contained in a 600 ml polythene beaker. After standing at room temperature for three hours, the solution was poured on to crushed ice (1 Kg). The organic material, separating as thick oil which set to a pale yellow oil, was dissolved in ether (1 litre) and the ether solution was washed successively with water (4 x 300 mls), 10% potassium hydroxide solution (2 x 500 mls) and water (2 x 300 mls) and dried (Na_2SO_4). Solvent was evaporated and the residual pale yellow oil was dissolved in boiling light petroleum (200 mls) and crystallisation allowed to proceed. The ketone (64 gms; 93%) was obtained as very pale yellow, almost colourless prisms, m.pt. 58.5-61°C. After two further crystallisations from light petroleum, the melting point was 61-62°C.

Analysis: Found C 85.83 H 7.08%

$C_{16}H_{16}O$ requires C 85.67 H 7.19%

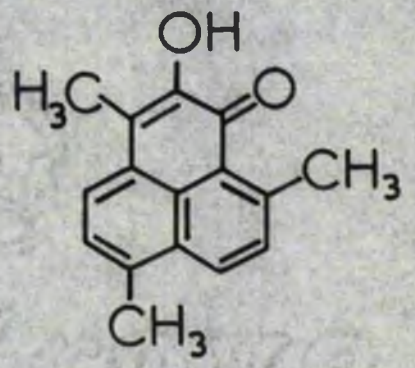
The 2,4-dinitrophenylhydrazone was prepared from the ketone (500 mgms) and 2,4-dinitrophenylhydrazine (440 mgms) in ethanol

containing concentrated hydrochloric acid (0.1 ml) and crystallisation was allowed to proceed from 20 mls solution. After two recrystallisations from ethanol, the compound formed red prisms, m.pt. 257-259°C with decomposition.

Analysis: Found N 14.0%

$C_{22}H_{20}O_4N_4$ requires N 13.88%

C.IX.9. 2-Hydroxy-5,6,9-trimethylperinaphthenone.



A solution of 5,6,9-trimethylperinaphthan-1-one (5.9 gms), p-nitrosodimethylaniline (2.7 gms) and potassium hydroxide (1 gm) in ethanol (100 mls) was allowed to stand for four hours at room temperature. One-half of the solvent was removed by distillation and the violet-black precipitate consisting of the azomethine derivative of 5,6,9-trimethylperinaphthan-1-one was filtered from the cooled solution. It was hydrolysed by boiling under reflux for five hours with aqueous: ethanolic hydrochloric acid (approximately 5 N; 100 mls). The cooled solution was poured into water (250 mls) and the dark brown precipitate was collected. This was dried and, after two sublimations

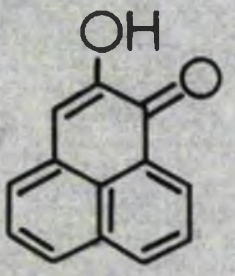
at 150-170°C / 0.1 m.m., gave the desired product as red prisms, which crystallised from ethanol as red needles (2.5 gms; 60%), m.pt. 168-171°C with decomposition.

Analysis: Found C 80.90 H 5.76%

$C_{16}H_{14}O_2$ requires C 80.65 H 5.92%

The carbonyl absorption band in the infra-red lay at 1608 cm^{-1}.

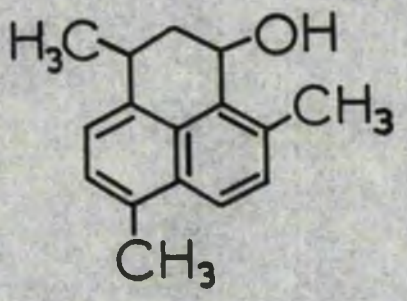
C.IX.10. 2-Hydroxyperinaphthenone.



A solution of perinaphthan-1-one (5.4 gms), p-nitrosodimethylaniline (5.4 gms) and potassium hydroxide (2 gms) in ethanol (200 mls) was allowed to stand at room temperature for four hours. The violet-black crystals of the azomethine compound which had crystallised were filtered off and hydrolysed by boiling under reflux for 2½ hours with a mixture of concentrated hydrochloric acid (75 mls) and ethanol (100 mls). The red precipitate which crystallised on cooling was purified by sublimation at 140-150°C / 0.1 m.m., followed by two crystallisations from benzene. The yield of 2-hydroxyperinaphthenone was 2 gms (30%) as red needles, m.pt. 184-185°C (lit 184-184.5°C[81] and 188-189°C[95]).

The carbonyl absorption band in the infra-red lay at 1618 cm^{-1}.

C.IX.ii. 3,6,9-Trimethylperinaphthan-1-ol (CCXV).



(CCXV)

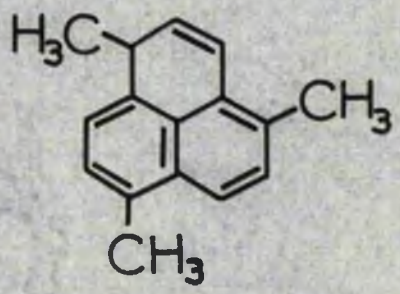
A solution of 3,6,9-trimethylperinaphthan-1-one (48 gms) in anhydrous ether (450 mls) was added to a suspension of lithium aluminium hydride (3.5 gms) in anhydrous ether (800 mls) at such a rate that the ether boiled gently. When addition was complete, external heat was applied and the mixture was boiled under reflux for a further hour. After cooling, it was poured into ice-cold 2 N sulphuric acid (1 litre). The ethereal layer was separated, washed with water (2 x 700 mls) and dried (Na_2SO_4). After evaporation of solvent, recrystallisation of the very pale yellow crystalline residue from a mixture of acetone and light petroleum (1:1) yielded a first crop of small colourless needles (36.5 gms), m.pt. 114-115°C. The concentrated mother liquors yielded a second crop which after two crystallisations from a mixture of acetone and light petroleum gave 8 gms, m.pt. 114-115°C, bringing the total yield of pure 3,6,9-trimethylperinaphthan-1-ol to 44.5 gms (92%). A sample prepared for analysis after one further

recrystallisation from a mixture of acetone and light petroleum melted at 115-115.5°C.

Analysis: Found C 85.06 H 7.84%

$C_{15}H_{16}O$ requires C 84.91 H 8.02%

9.IX.12. 1.4.7-Trimethylperinaphthene (CCIV): First experiment.



(CCIV)

Absolute ethanol (80 mls), saturated with hydrogen chloride gas, was added to a solution of 3,6,9-trimethylperinaphthan-1-ol (10 gms) in absolute ethanol (50 mls). The resulting solution was boiled under reflux for forty five minutes during which time the colour changed from pale yellow to a very dark green. The cooled solution was poured into water (1½ litres), the aqueous mixture was extracted with light petroleum (2 x 500 mls) and the light petroleum solution was washed well with water (6 x 250 mls) and dried (Na_2SO_4). Removal of the solvent and distillation of the residual brown oil at 0.5 m.m. yielded a blue-green oil (5.94 gms; 65%) which, on trituration with light petroleum, solidified to colourless needles, m.pt. 40-42°C. One recrystallisation from light petroleum raised the melting point to

47-51°C and, after a further recrystallisation from light petroleum containing a trace of acetone, the melting point was 85-90°C.

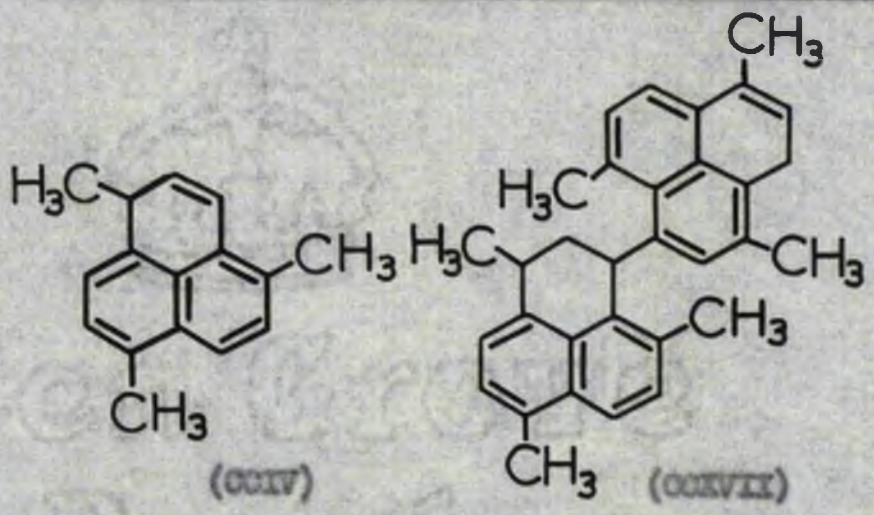
Analysis: Found C 92.02 H 7.74%

M.W. 197

$C_{16}H_{16}$ requires C 92.26 H 7.75%

M.W. 208

C.IX.13. 1,4,7-Trimethylperinaphthene (CCIV): Subsequent experiments.



(CCIV) (CCXVII)

Absolute ethanol (50 mls), saturated with hydrogen chloride gas, was added to a solution of 3,6,9-trimethylperinaphthan-1-ol (10 gms) in absolute ethanol (50 mls). The resulting solution was boiled under reflux for forty-five minutes before being poured into water (1½ litres). The aqueous mixture was extracted with light petroleum (750 mls) and the resulting extract was washed with water (6 x 250 mls) and dried (Na_2SO_4). After concentration to a volume of 50 mls, it was passed down a column of alumina (20 x 4 cms) using light petroleum as eluting solvent. Solvent was evaporated from the eluate (1 litre) and light

petroleum (10 mls) was added to the residue. The colourless needles which crystallised were removed by filtration, solvent evaporated from the light petroleum solution and the residue distilled at 150°C / 0.1 m.m. The distillate was used as such in the reactions carried out on 1,4,7-trimethylperinaphthenone.

A sample of the distillate (210 mgms) in a mixture of ethanol (2 mls) and benzene (2 mls) was treated with a solution of trinitrobenzene (215 mgms) in ethanol (5 mls). The brick-red complex which precipitated was removed by filtration and was divided into two parts. The first part crystallised from acetone in red needles, m.pt. above 250°C; the second part was recrystallised from benzene, forming red needles, which melted above 330°C. Although the complex is stated to melt above 330°C, it started to darken about 140°C, becoming black at 200°C, but its crystalline form was maintained above 330°C.

Analysis: Found C 63.34 H 4.58 N 10.83%

$C_{22}H_{19}N_3O_6$ requires C 62.70 H 4.54 N 9.97%

The crystalline solid (71 mgms) which had been filtered off before distillation, crystallised from benzene as colourless needles, m.pt. 237-239°C. This compound is considered to have a structure akin to (CCXVII).

Analysis: Found C 92.56 H 7.27% M.W. 231

$C_{32}H_{30}$ requires C 92.72 H 7.30% M.W. 415

C,IX,14. Dehydration of 5,6,9-trimethylperinaphthan-1-ol using phosphorus pentoxide in benzene.

5,6,9-Trimethylperinaphthan-1-ol (4.50 gms) was added to a solution of phosphorus pentoxide (4.50 gms) in benzene (60 mls) and the resulting solution was allowed to stand at room temperature for thirty minutes. A further quantity of phosphorus pentoxide (5 gms) was added and the mixture was shaken for one hour before being poured into water (250 mls). The organic material was extracted into ether (200 mls), the ether extract was washed successively with water (2 x 200 mls), saturated sodium bicarbonate solution (200 mls) and water (200 mls) and dried (Na_2SO_4). Solvent was removed by distillation and the residual oil was dissolved in a mixture of benzene (10 mls) and light petroleum (20 mls). This solution was passed down a column of alumina (10 cm x 4 cm) using light petroleum as eluting solvent. The eluate (200 mls), after concentration to a volume of 12 mls, gave 130 mgms of pale yellow, almost colourless needles. After five crystallisations from benzene, the compound formed colourless needles, m.pt. 257-259°C. This compound did not depress the melting point of (COMPLEX), obtained in C,IX,13.

Further development of the chromatographic column using benzene as eluting solvent yielded only brown intractable tars from which no useful product could be isolated.

C.X. Attempted Oxidations of 1,4,7-Trimethylperinaphthene.

C.X.1. Attempted oxidation of 1,4,7-trimethylperinaphthene: using chromic anhydride.

1,4,7-Trimethylperinaphthene (500 mgms) was added to a solution of chromium trioxide (350 mgms) in acetic acid (15 mls) and the mixture was shaken at room temperature for ten minutes. The resulting green solution was then poured into water (250 mls) and the aqueous mixture was extracted with ether (2 x 150 mls). The ether extract was washed with water (2 x 150 mls), saturated sodium bicarbonate solution (150 mls), water (150 mls) and dried (Na_2SO_4). After evaporation of solvent, a dark brown tarry oil (400 mgms) remained from which no useful product could be obtained. After the oil had been standing in solution in a mixture of acetone and light petroleum (1:1) for some days, a dark brown solid (50 mgms) was filtered off. A green residue was left after ignition, suggesting the presence of chromium, but efforts to further purify the material were of no avail.

C.X.2. Attempted oxidation of 1,4,7-trimethylperinaphthene: using sodium dichromate.

A solution of the hydrocarbon (350 mgms) in glacial acetic acid

(5 mls) was added to a solution of $Na_2Cr_2O_7.2H_2O$ (1 gm) in acetic acid (25 mls) and the mixture was boiled under reflux for thirty minutes. A dark brown, inorganic, ether insoluble product was obtained on cooling the solution. No useful product could be obtained from this, nor from the acetic acid filtrate.

C.K.5. Attempted oxidation of 1.4.7-trimethylperinaphthene: using p-nitrosodimethylaniline.

A solution of p-nitrosodimethylaniline (300 mgms) in ethanol (6 mls) was added to a solution of the hydrocarbon (406 mgms) in ethanol(40mls). The dark green solution was brought to the boiling-point in an atmosphere of nitrogen and a solution of sodium (46 mgms) in ethanol (4 mls) was added. The solution became very dark brown and was boiled for two minutes, then cooled and poured into water (250 mls). The aqueous mixture was extracted with ether (250 mls) and the ether extract was washed with water (6 x 150 mls) and dried (Na_2SO_4). Removal of solvent left a high boiling, dark red oil which could not be further purified or characterised.

C,XI. Attempts to form the Trimethylperinaphthenide Anion.

C,XI,1. The use of potassium methoxide.

Reaction of 1,4,7-trimethylperinaphthene with potassium methoxide in 2% ethanolic ether solution under the conditions described above (C,IV,1) for the formation of the perinaphthenide anion yielded unchanged hydrocarbon.

C,XI,2. The use of butyl lithium.

A solution of butyl lithium was prepared from lithium wire (850 mgms) and n-butyl bromide (6.6 gms) in ether (40 mls) in an atmosphere of dry nitrogen, as described by Gilman[194].

A solution of 1,4,7-trimethylperinaphthene (500mgms) in ether (5 mls) was added to the above solution of butyl lithium (5 mls) in an atmosphere of dry nitrogen. The mixture was pale yellow and retained this colour after being boiled under reflux for six hours. On pouring the cooled solution into water and working up the organic layer in the usual way, unchanged 1,4,7-trimethylperinaphthene (400 mgms) was obtained.

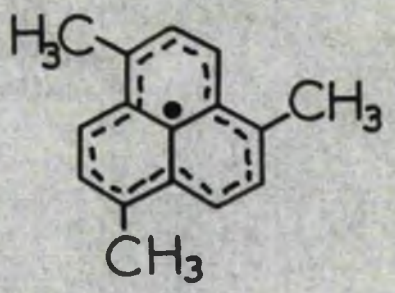
C.XI.3. The use of ethyl magnesium bromide.

A solution of ethyl magnesium bromide was prepared from ethyl bromide (1.52 mls) and magnesium turnings (510 mgms) in ether (50 mls)

To a portion of this solution (6 mls), contained in a 100 mls flask fitted with a dropping funnel and a reflux condenser and carrying a nitrogen inlet tube, was added a solution of 1,4,7-trimethylperinaphthene (510 mgms) in ether (25 mls) and the resulting solution was boiled under reflux. This produced no colour change; the ether was therefore removed by distillation and replaced by toluene. There was no indication of the formation of the anion of 1,4,7-trimethylperinaphthene even after four hours' boiling under reflux.

C.XII. The Radical and Cation derived from 1,4,7-Trimethylperinaphthene.

C.XII.1. 1,4,7-Trimethylperinaphthyl: Preparation.



(CXXXIV)

N-Bromosuccinimide (2.70 gms; 5% excess) was added to a solution of 1,4,7-trimethylperinaphthene (2.96 gms) in carbon tetrachloride (100 mls) and the solution was boiled under reflux for seventy-five minutes. The solution, originally pale yellow in colour, gradually turned dark green. After cooling, it was passed through a column of alumina (15 x 3.2 cms) using ether as eluting solvent. The eluate (400 mls) was greenish-yellow in colour and turned an intense blue on warming; it was concentrated to a volume of 50 mls and this solution was rechromatographed on alumina (10 x 3.2 cms) using ether as eluting solvent. 1,4,7-Trimethylperinaphthyl was thus obtained as a violet blue entity in the first 250 mls of eluate. The blue colour faded gradually and the solution turned yellow when it was allowed to stand at room temperature. 1,4,7-Trimethylperinaphthyl was stable in methyl-naphthalene at the boiling point (240°C).

C.XXI.2. 1,4,7-Trimethylperinaphthyl: Reaction with iodine.

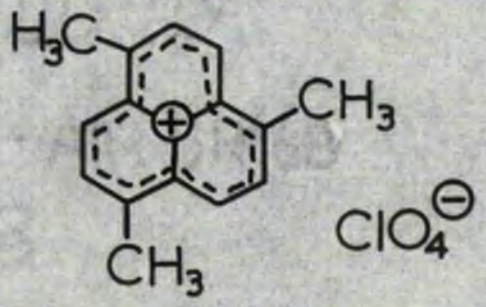
An ethereal solution of 1,4,7-trimethylperinaphthyl, obtained as described above, was treated dropwise with a solution of iodine in benzene (10 mls; approximately 2 gms iodine per 150 mls benzene). The violet blue colour of the radical was discharged and the black solid (30 mgms) which was formed was filtered off and washed with small volumes of benzene and light petroleum. This compound was soluble in pyridine yielding a green solution.

Analysis: Found C 41.50, 43.91 H 2.95, 5.12% I 55.69, 53.8%

$C_{16}H_{15}I$ requires C 57.50 H 4.32 I 37.98%

$C_{16}H_{15}I_2$ requires C 41.07 H 3.28 I 55.05%

C.XXI.3. 1,4,7-Trimethylperinaphthenylium perchlorate.



(CXXXVIII)

A solution of triphenylmethyl perchlorate (1.75 gm) in glacial acetic acid (200 mls) was added to a solution of 1,4,7-trimethyl-

perinaphthene (1.06 gm) in glacial acetic acid (300 mls). 1,4,7-Trimethylperinaphthenylium perchlorate began to crystallise almost immediately as yellow needles (370 mgm; 37%). These were filtered off after five minutes, washed with ether (50 mls) and light petroleum (25 mls) and dried in vacuo over phosphorus pentoxide. The compound crystallised from acetonitrile as copper coloured needles which decomposed above 260°C.

Analysis: Found C 63.72, 63.26 H 5.14, 5.33%
Cl 11.0, 11.1%

$C_{16}H_{15}ClO_4$ requires C 62.65 H 4.93 Cl 11.56%

C.XIII. Dehydrogenations using the Triphenylmethyl Carbonium Ion.

C.XIII.1. Preparation of triphenylmethyl perchlorate.[193]

A solution prepared by dissolving triphenylmethyl chloride (10.8 gms)[193] in dry, freshly distilled nitrobenzene (30 mls) at 80°C, was added to a solution of silver perchlorate (thoroughly dried at 110° and stored at reduced pressure over phosphorus pentoxide) (8.2 gms) in nitrobenzene (90 mls) at 150° with vigorous swirling. The solution becomes deep yellow at once and a heavy precipitate of silver chloride was deposited. This was filtered off at once, dry benzene (20 mls) added to the filtrate to precipitate silver chloride completely and the mixture again filtered after warming, if necessary, to redissolve the triphenylmethyl perchlorate which had begun to crystallise. The filtrate was warmed to 80° and dry benzene (250-300 mls) was added at its boiling point. The perchlorate began to crystallise and the mixture was allowed to come to room temperature spontaneously (1 hour). It was then further chilled in cold water at 5-10° for 2½ hours before filtration. The perchlorate was filtered as rapidly as possible, washed with dry benzene followed by dry light petroleum and dried in vacuo over phosphorus pentoxide. The yield was 8 gms (60%).

C.XIII.2. Dehydrogenation of perinaphthan-1-one.

A solution of perinaphthan-1-one (304 mgms) in glacial acetic acid (5 mls) was added to a suspension of triphenylmethyl perchlorate (686 mgms) in glacial acetic acid (25 mls) and the mixture was boiled under reflux until solution was complete (ten minutes). After cooling, the solution was poured into water (250 mls) and the organic material was extracted into benzene (2 x 100 mls). Perinaphthenone was extracted from the benzene solution in the usual manner using concentrated hydrochloric acid and subsequently purified by sublimation at 150°C / 0.5 m.m. followed by recrystallisation from a mixture of benzene and petroleum ether. The product was obtained as yellow needles (290 mgms; 96%), m.pt. and mixed m.pt. with an authentic sample of perinaphthenone, 155.5 - 156.5°C.

The benzene solution from which perinaphthenone had been extracted was washed with water (2 x 100 mls), saturated sodium bicarbonate solution (150 mls) and water (100 mls) and dried (Na_2SO_4). Solvent was removed and the residue recrystallised twice from ethanol yielding triphenylmethane (300 mgms; 62%) as colourless needles, m.pt. 93-94°C (lit 94°C).

C.XIII.3. Dehydrogenation of 3,6,9-trimethylperinaphthan-1-one.

A suspension of triphenylmethyl perchlorate (686 mgms) in glacial

acetic acid (45 mls) was added to a solution of 3,6,9-trimethylperinaphthen-1-one (446 mgms) also in glacial acetic acid (5 mls). The mixture was boiled under reflux until solution was complete (fifteen minutes), cooled, poured into water (250 mls), and the organic material extracted into benzene (2 x 100 mls). 3,6,9-Trimethylperinaphthenone was extracted from the benzene solution using concentrated hydrochloric acid (4 x 50 mls). The acid extract was diluted with four times its volume of water and the resulting emulsion was extracted with benzene (2 x 200 mls). The benzene solution was washed with water (200 mls), saturated sodium bicarbonate solution (200 mls) and water (200 mls) and dried (Na_2SO_4). After removal of the solvent by distillation, the residue was sublimed at 150°C / 0.1 m.m. yielding 3,6,9-trimethylperinaphthenone (360 mgms; 81%) which crystallised from petroleum ether as yellow needles, m.pt. 106-107°C.

Analysis: Found C 86.57 H 6.40%

$C_{16}H_{14}O$ requires C 86.44 H 6.35%

The benzene solution, which had been extracted with acid, was washed with water (2 x 200 mls), saturated sodium bicarbonate solution (200 mls) and water (200 mls) and dried (Na_2SO_4). The residue obtained after removal of solvent yielded, after one recrystallisation from ethanol, triphenylmethane (340 mgms; 70%) as colourless needles, m.pt. 93.5-94°C.

C.XIII.4. Dehydrogenation of 9:10-dihydroanthracene.

Triphenylmethyl perchlorate (343 mgms) was added to a solution of 9:10-dihydroanthracene (180 mgms) in glacial acetic acid (10 mls) and the mixture was brought to the boiling point. The solution became yellow-green in colour and, finally, green as the triphenylmethyl perchlorate went into solution. Boiling under reflux was continued for four minutes during which time the colour changed from yellow-green, through deep green to pale green, almost colourless. Anthracene (160 mgms; 90%) crystallised from the cooled solution as plates, m.pt. 215-218°C with sublimation.

C.XIII.5. Dehydrogenation of dihydroindeno[2,1-a]-perinaphthene[129]

A solution, prepared by dissolving triphenylmethyl perchlorate (160 mgms) in acetic acid (40 mls) and cooling below 20°, was added to a solution of dihydroindeno[2,1-a]-perinaphthene (120 mgms) in acetic acid (10 mls), also cooled below 20°. The resulting solution became red at once. It was allowed to stand at room temperature (15°) for three hours during which time a brown microcrystalline solid separated from solution. This solid (60 mgms) was removed by filtration and was worked up separately from the mother liquors and recrystallised from a mixture of benzene and light petroleum (4 : 1). It dissolved in benzene and acetone yielding deep red solutions and is

12-triphenylmethyl-indeno[2,1-a]-perinaphthene, melting above 300°C.

Analysis: Found C 94.91 H 4.66%

$C_{39}H_{28}$ requires C 94.69 H 5.31%

The mother liquors were poured into water (300 mls) and extracted with benzene (2 x 75 mls). The benzene extract was washed free of acetic acid and extracted with 77% sulphuric acid (3 x 100 mls). The acid extracts, diluted by pouring into water (1700 mls), were extracted with ether and the red ether extract was washed free of sulphuric acid using water (four times), saturated sodium bicarbonate solution (twice), and water (twice), in succession, before drying (K_2CO_3) and removal of the solvent. The residue was dissolved in benzene and passed through a short column of alumina (3 x 2.7 cms) using benzene as eluting solvent. After concentration of the eluate to low volume, a solution of trinitrobenzene in ethanol was added. The trinitrobenzene complex of indeno[2,1-a]-perinaphthene crystallised as brown needles (20 mgms), m.pt. 175-176°C (lit[139] 175-176°C).

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LITERATURE CITED.

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Austral.J.Chem.	Australian Journal of Chemistry.
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Ber.	Berichte der deutschen chemischen Gesellschaft (discontinued with vol. 77,1944; continued as Chemische Berichte with vol. 80, 1947).
Bull. Acad. Sci.	Bulletin de l'Académie des Sciences de l'U.R.S.S.
Bull. soc.	Bulletin de la société chimique de France.
Can. Res.	Journal of Cancer Research.
Clar.	Clar, "Aromatische Kohlenwasserstoffe", 2nd. Edition, Springer-Verlag, Berlin, 1952.
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Compt.rend.Acad.Sci.	Comptes rendus de l'Académie des Sciences de l'U.R.S.S.
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Chem. Zentr.	Chemisches Zentralblatt.
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D.R.P.	Deutsche Reichspatente.
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Gazz. chim. Ital.	Gazzetta chimica Italiana.
J.A.C.S.	Journal of the American Chemical Society.
J.Biol. Chem.	Journal of Biological Chemistry.
J.C.S.	Journal of the Chemical Society.
J.Chem. Phys.	Journal of Chemical Physics.
J.Gen. Chem.	Journal of General Chemistry (U.S.S.R.)New York. (U.S. translation of Zhurnal obshchei Khimii).
J. Ind.Chem. Soc.	Journal of the Indian Chemical Society.
J. Org. Chem.	Journal of Organic Chemistry.
J.prakt. Chem.	Journal für praktische Chemie (discontinued after vol. 162, 1943.)
Monatsh.	Monatshefte für Chemie.
Naturwiss.	Naturwissenschaften.
Org. Reactions.	Organic Reactions.
Org. Synth.	Organic Syntheses.
Rev. sci.	La Révue scientifique.
Stelzner.	Stelzner, "Literatur-Register der Organischen Chemie".
Tetrahedron.	Tetrahedron. International Journal of Organic Chemistry.
Trans. Faraday Soc.	Transactions of the Faraday Society.
U.S.P.	United States Patent.
Z.Elektrochem.	Zeitschrift für Elektrochemie.
Z. Physik.	Zeitschrift für Physik.

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PLATES

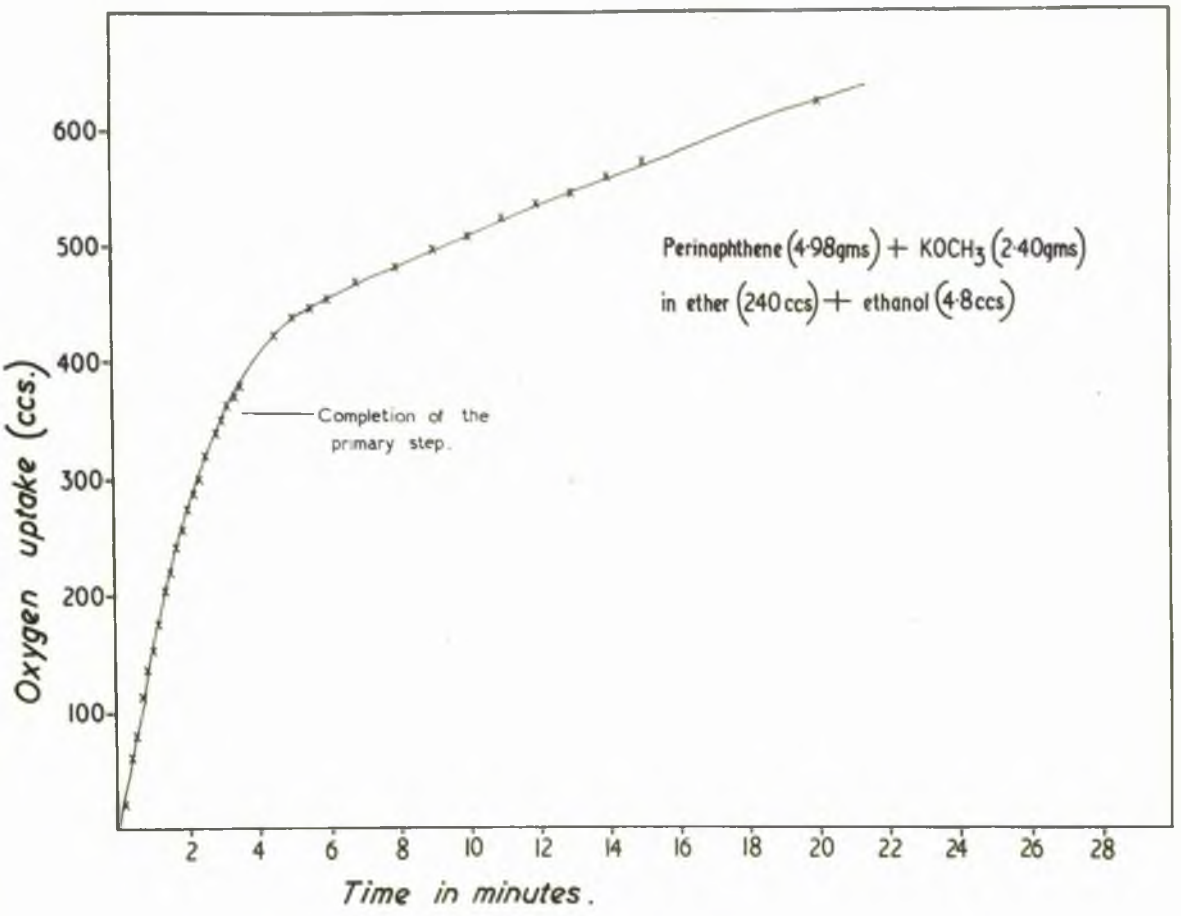

PLATE I. Oxygenation of the perinaphthenide anion.

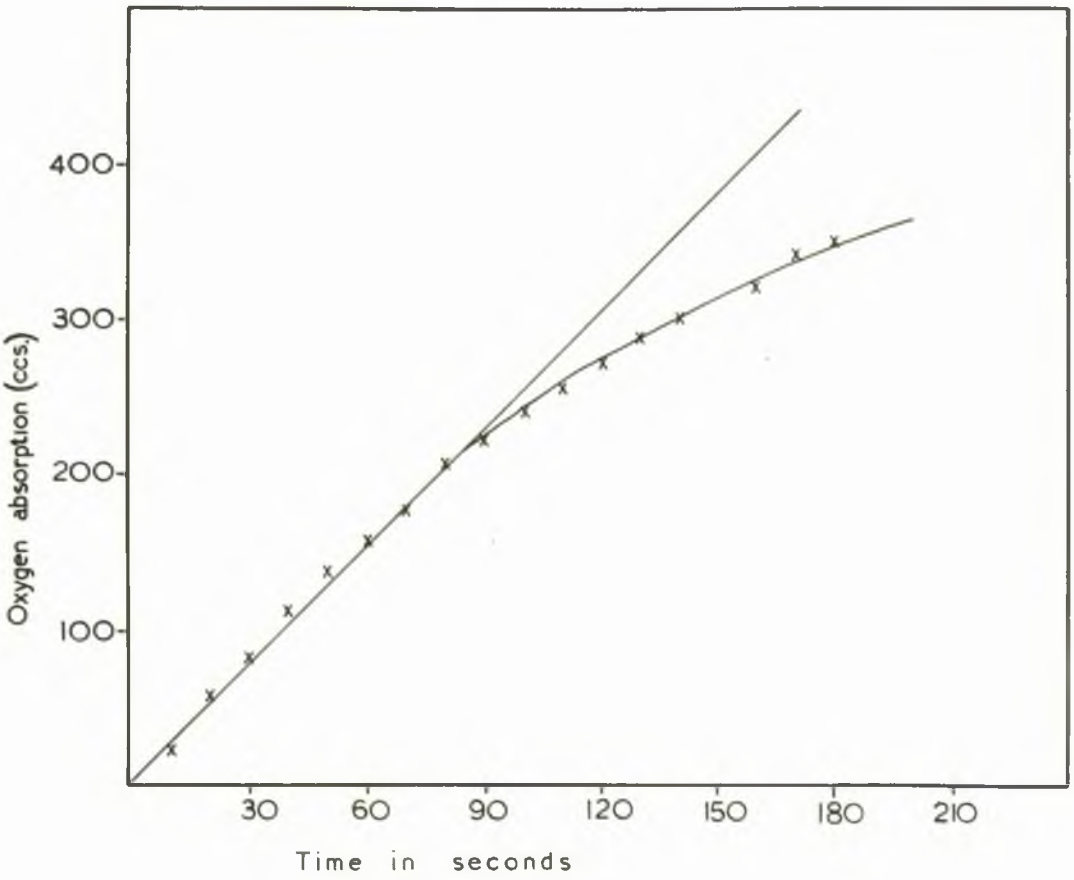

PLATE II. Oxygenation of the perinaphthenide anion.

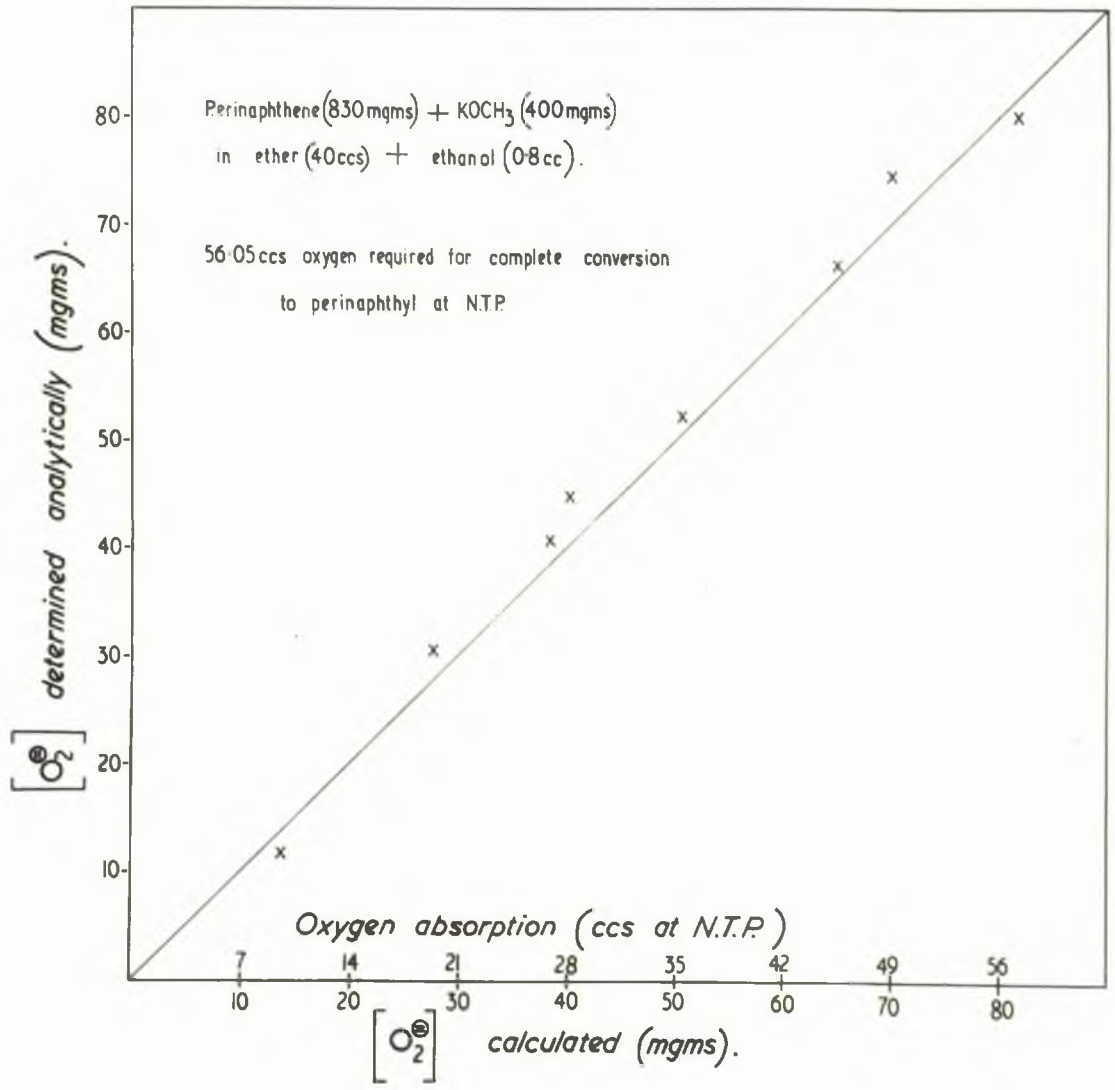

PLATE III. Oxygenation of the perinaphthenide anion.

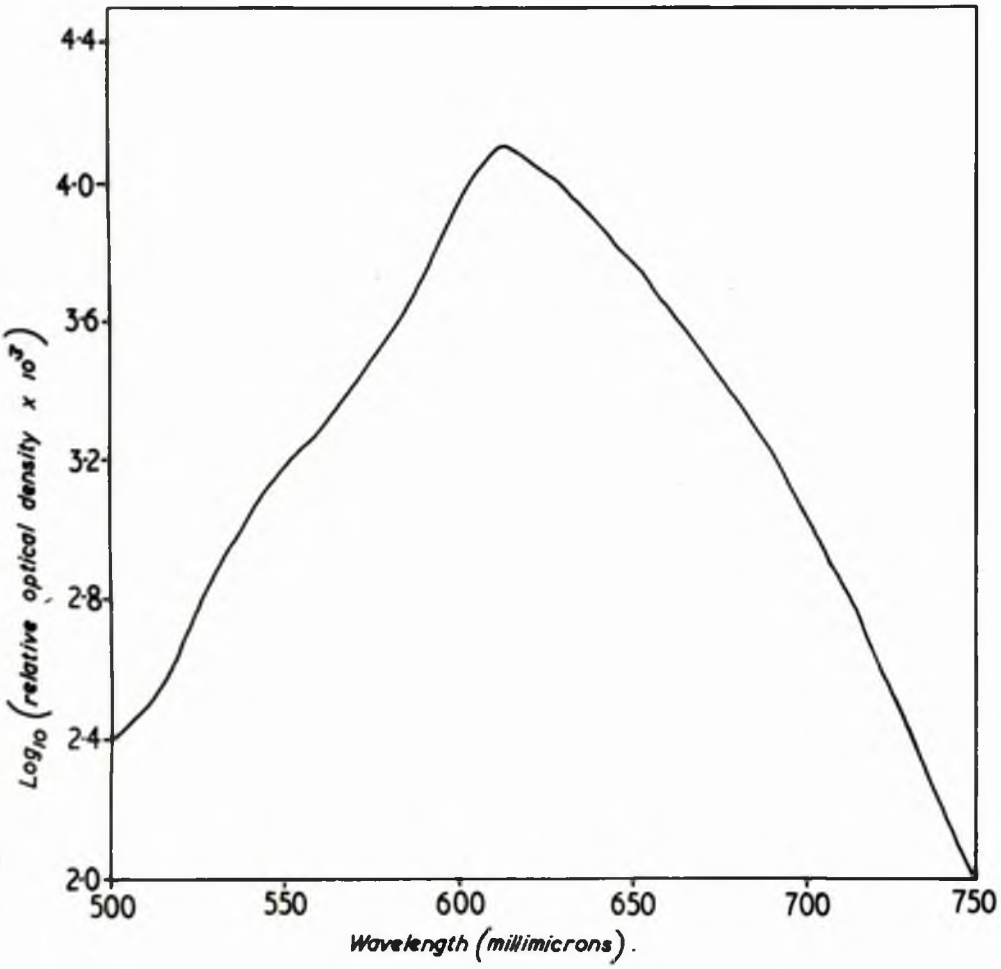

PLATE IV. Absorption spectrum of perinaphthyl in ether.

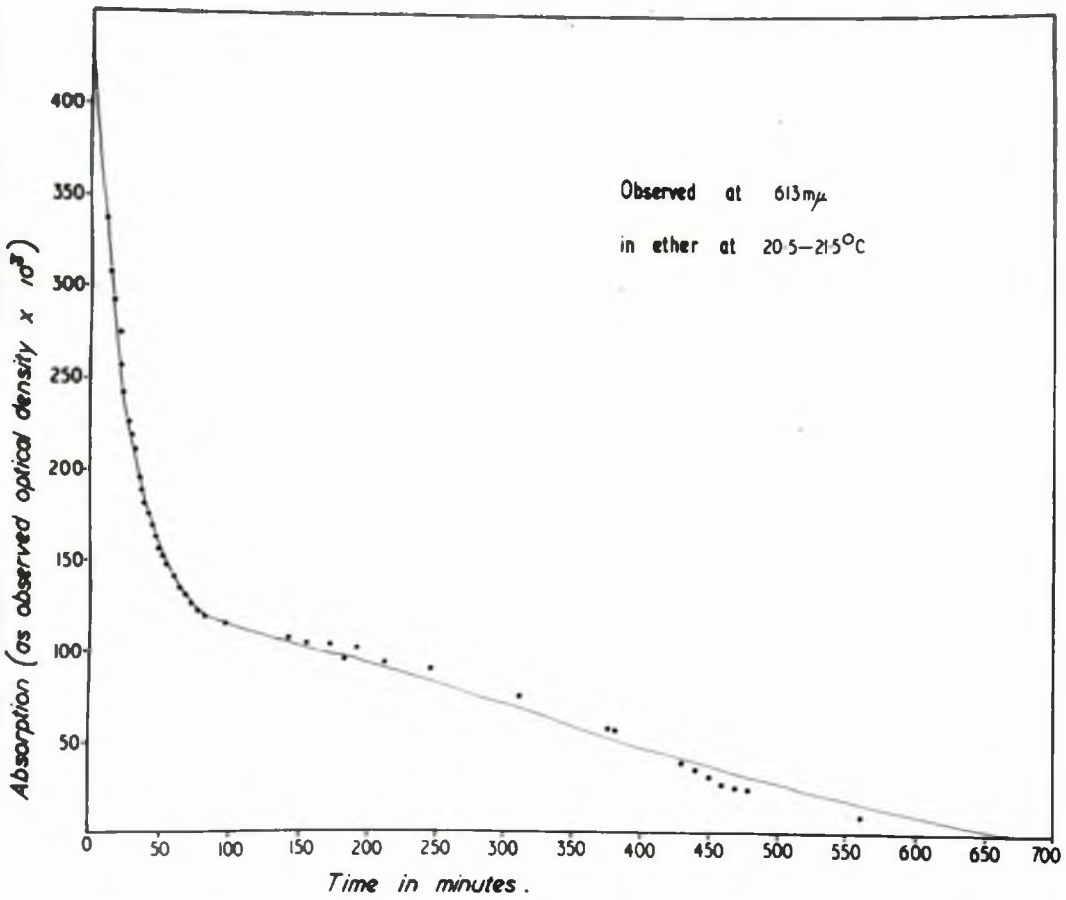

PLATE V. Dimerisation and disproportionation of perinaphthyl.

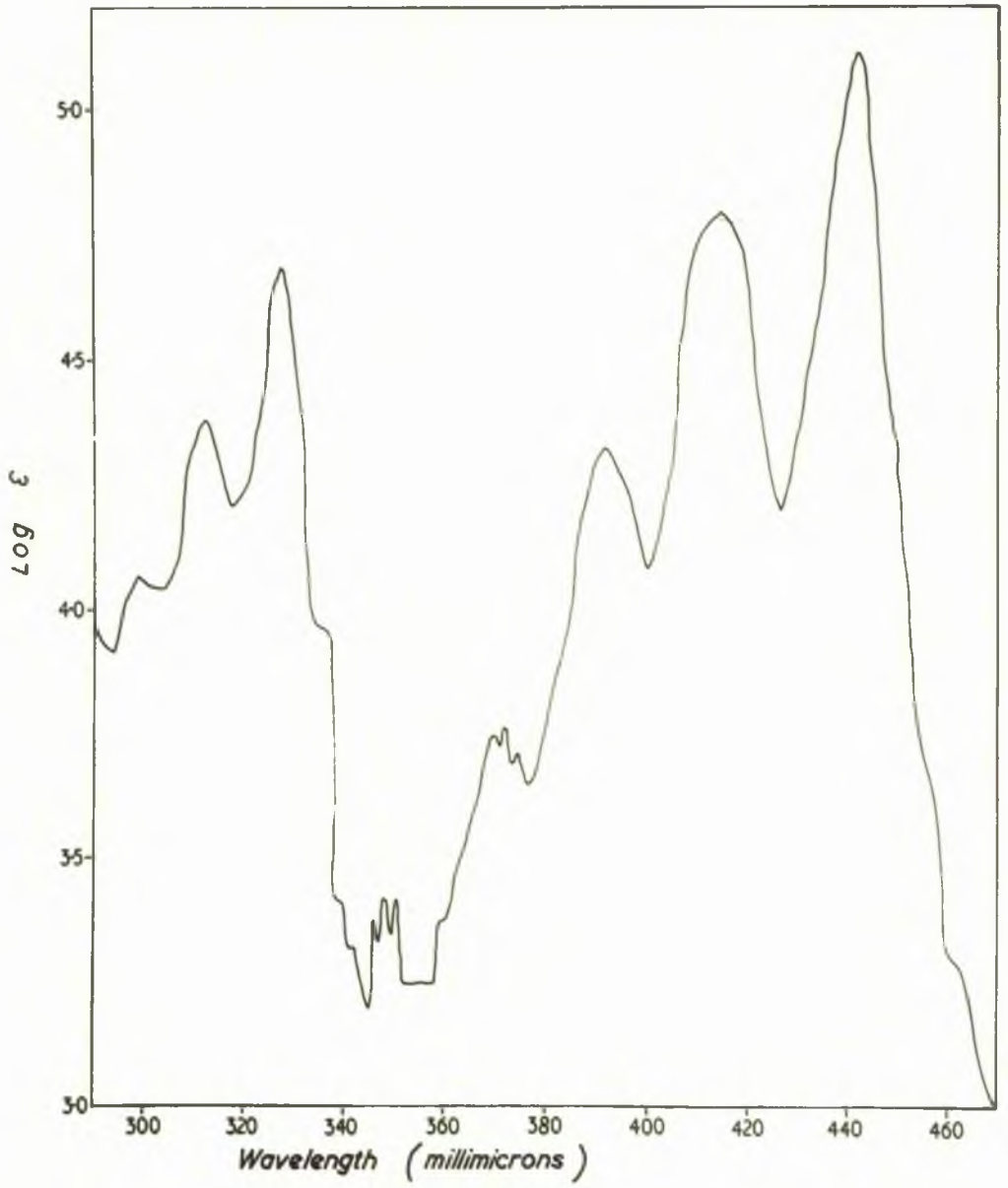

PLATE VI. Absorption spectrum of peropyrene in benzene.